Total Synthesis of Ritterazine B

Yasuaki Nakayama[‡], Michael R. Maser[‡], Tatsuya Okita, Anton V. Dubrovskiy, Taryn L. Campbell, and Sarah E. Reisman

The Warren and Katharine Schlinger Laboratory for Chemistry and Chemical Engineering
Division of Chemistry and Chemical Engineering, California Institute of Technology
Pasadena, California 91125, United States
reisman@caltech.edu

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1. General Procedures

Synthetic details:
Unless otherwise stated, reactions were performed under a nitrogen atmosphere using freshly dried solvents utilizing standard Schlenk techniques. Tetrahydrofuran (THF), methylene chloride (CH_2Cl_2/DCM), diethyl ether (Et_2O), benzene (PhH) and toluene (PhMe) were dried by passing through activated alumina columns. Dichloroethane ($(CH_2Cl)_2$/DCE), triethylamine (Et_3N), and isopropanol (*i*-PrOH) were distilled over calcium hydride prior to use. 2,6-lutidine and 3-butyn-2-ol were distilled by short-path distillation at ambient pressure prior to use. Unless otherwise stated, chemicals and reagents were purchased from Sigma-Aldrich and used as received. Glassware was oven-dried at 120 °C for a minimum of four hours, or flame-dried utilizing a Bunsen burner under high vacuum. All reactions were monitored by thin-layer chromatography using EMD/Merck silica gel 60 F254 pre-coated plates (0.25 mm) and were visualized by UV (254 nm), *p*-anisaldehyde staining. Flash column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40-63 microns [230 to 400 mesh]) purchased from Silicycle. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD with Prodigy Cryoprobe (at 400 MHz and 101 MHz, respectively) or a Varian Inova 500 (at 500 MHz and 101 MHz respectively) and are reported relative to internal $CHCl_3$ (^{1}H, δ = 7.26) and $CDCl_3$ (^{13}C, δ = 77.0), C_6H_6 (^{1}H, δ = 7.16) and C_6D_6 (^{13}C, δ = 128), or C_5H_5N (^{1}H, δ = 8.74, 7.58, 7.22) and C_5D_5N (^{13}C, δ = 150.35, 135.91, 123.87). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS were acquired from the Caltech Mass Spectral Facility using fast-atom bombardment (FAB), electrospray ionization (ES+-TOF) or electron impact (EI). Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm. Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system with a Chiralcel AD-H column (4.6 mm x 25 cm).

Computational details:
DFT optimizations and energy evaluations were performed using the Entos Qcore software package v0.8.14 on Entos clusters hosted on their academic JupyterHub servers. We thank Entos for providing access to these servers. Optimized structure visualizations in the main text and in this document were generated using Avogadro from the .xyz coordinate files obtained from Entos outputs. Si protecting groups were removed from these renderings for clarity, but were present in the calculations. All optimizations and energy evaluations were conducted at the BLYP/6-31G** level of theory.

2. Synthetic Procedures

2i. Synthesis of α-hydroxy ketone 12

Preparation of imine S1[1]:

A 250 mL round-bottom flask with a stir bar was equipped with a Dean–Stark apparatus and reflux condenser and was charged with *trans*-dehydroandrosterone (**8**, 10.0 g, 34.7 mmol), 2-aminomethyl pyridine (10.7 mL, 104 mmol, 3.0 equiv), *p*-TsOH (150 mg, 867 μmol, 2.5 mol %) and toluene (87 mL, 0.4 M). The resulting solution was heated to reflux for 8 h. After cooling to ambient temperature, the reaction was diluted with $CHCl_3$ (80 mL), quenched with st. $NaHCO_3$ aq. (40 mL). The layers were separated, and the aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were washed with brine (50 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was disolved in a minimal amount of acetone and diluted with hexane to precipitate out the product. The resulting solid

was collected by filtration to afford imine **S1** (11.6 g, 89% yield) as a white solid. Spectroscopic data were identical to those reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (m, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.13 (m, 1H), 5.37 (d, *J* = 5.1 Hz, 1H), 4.60 (q, *J* = 16.5 Hz, 2H), 3.52 (m, 1H), 2.53 – 2.43 (m, 1H), 2.36 – 2.29 (m, 2H), 2.26 (m, 1H), 2.07 (m, 2H), 1.92 – 1.87 (m, 1H), 1.87 – 1.81 (m, 2H), 1.73 – 1.60 (m, 3H), 1.60 – 1.53 (m, 1H), 1.53 – 1.44 (m, 2H), 1.41 (dd, *J* = 12.6, 3.9 Hz, 1H), 1.19 (m, 1H), 1.11 (dd, *J* = 13.3, 3.8 Hz, 1H), 1.04 (s, 3H), 1.03 – 0.98 (m, 1H), 0.92 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.08, 141.22, 136.74, 121.78, 121.75, 121.24, 71.76, 58.01, 53.41, 50.62, 45.81, 42.40, 37.37, 36.81, 34.15, 31.77, 31.67, 31.42, 28.25, 23.48, 20.88, 19.59, 16.36.

Preparation of diol 9[1]:

A 500 mL round-bottom flask with a stir bar was charged with imine **S1** (10.0 g, 26.4 mmol), $Cu(NO_3)_2$•$3H_2O$ (7.02 g, 29.1 mmol, 1.1 equiv) and THF (130 mL, 0.2 M). The heterogeneous mixture was stirred vigorously for 45 min at room temperature, and then 50 °C for 30 min to give a pale blue precipitate. After cooling to room temperature, hydrogen peroxide (13.5 mL, 132 mmol, 5.0 equiv, 30 wt % in H_2O) was then added to the reaction mixture dropwise which resulted in the dissolution of the precipitate to give a deep blue solution. This was accompanied by a slight exotherm and formation of gas. The reaction mixture was then stirred for 3 h at room temperature. Then, EtOAc (100 mL) and saturated aqueous Na_4EDTA (22.1 g, 58.1 mmol, 2.2 equiv in 100 mL of H_2O) were added, and the reaction mixture was stirred for 21 h. The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 200 mL), combined organic layers were washed with 1 N HCl aq. (2 × 100 mL), st. $NaHCO_3$ aq. (100 mL), brine (2 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was triturated with Et_2O (50 mL) and the resulting solid was collected by filtration, washed with Et_2O (50 mL), dried under high vacuum to give diol **9** (5.28 g, 17.3 mmol, 66% yield, two steps) as a white solid. The Et_2O residue was concentrated in vacuo, and subjected to flash column chromatography (50 to 75% EtOAc/hexanes) to afford diol **9** (800 mg, 2.62 mmol, 10% yield, two steps) as a white solid. This material was combined with that from trituration to give **9** (6.08 g, 19.9 mmol, 84% yield, single step). Spectroscopic data were identical to those reported in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38 (dt, *J* = 5.0, 1.8 Hz, 1H), 3.81 (ddd, *J* = 11.3, 4.7, 1.3 Hz, 1H), 3.51 (m, 1H), 3.08 (d, *J* = 1.4 Hz, 1H), 2.54 – 2.42 (m, 1H), 2.33 (ddd, *J* = 13.1, 5.1, 2.2 Hz, 1H), 2.24 (m, 1H), 2.18 – 2.06 (m, 2H), 2.04 – 1.95 (m, 1H), 1.87 (m, 1H), 1.85 – 1.82 (m, 1H), 1.80 (t, *J* = 4.7 Hz, 1H), 1.72 – 1.65 (m, 1H), 1.64 (m, 1H), 1.61 (m, 1H), 1.57 – 1.54 (m, 1H), 1.53 – 1.48 (m, 1H), 1.47 – 1.40 (m, 1H), 1.29 – 1.21 (m, 1H), 1.16 – 1.08 (m, 2H), 1.04 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.14, 120.90, 72.81, 71.68, 51.53, 49.67, 49.25, 42.23, 37.28, 36.91, 35.90, 31.69, 30.71, 30.51, 28.33, 21.84, 19.49, 8.20.

Note: The C17 ketone ^{13}C signal is known to appear at 222 ppm.[2] The scan width of the ^{13}C experiment does not reach this chemical shift and thus the peak is absent; the remainder of the spectrum is identical to that reported in ref 2.

Preparation of α-bromo ketone 10:

A 1 L round-bottom flask with a stir bar was charged with diol **9** (14.0 g, 46.0 mmol), Et_3N (48.1 mL, 345 mmol, 7.5 equiv) and CH_2Cl_2 (230 mL, 0.2 M). TBSOTf (52.8 mL, 230 mmol, 5.0 equiv) was added at room temperature. After stirring at room temperature for 30 min, the reaction was cooled to 0 °C stirred at this temperature for 15 min. Thereafter, *i*-PrOH (10.6 mL, 138 mmol, 3.0 equiv) was added. After stirring at 0 °C for 30 min, NBS (16.4 g, 92.0 mmol, 2.0 equiv) was added in one portion and stirred at 0 °C for 30 min. The reaction was diluted with hexane (200 mL), quenched with H_2O (200 mL). The layers were separated. The aqueous layer was further extracted with hexane (3 × 200 mL), combined organic layers were washed with st. $NaHCO_3$ aq. (200 mL), brine (2 × 200 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography (5 to 7 to 10% Et_2O/hexanes) to afford α-bromo ketone **10** (27.3 g, 44.7 mmol, 98% yield) as a colorless foam.

TLC (10% Et_2O/hexanes): R_f = 0.50 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.33 (dt, *J* = 5.5, 1.8 Hz, 1H), 4.50 (dd, *J* = 6.9, 1.7 Hz, 1H), 3.80 (dd, *J* = 10.7, 4.9 Hz, 1H), 3.48 (m, 1H), 2.31 – 2.26 (m, 1H), 2.24 (m, 1H), 2.23 – 2.17 (m, 2H), 2.04 (ddd, *J* = 12.4, 5.2, 2.6 Hz, 1H), 1.82 – 1.73 (m, 2H), 1.71 (t, *J* = 4.9 Hz, 1H), 1.68 – 1.65 (m, 1H), 1.65 – 1.58 (m, 2H), 1.44 (m, 1H), 1.15 – 1.05 (m, 2H), 1.02 (s, 3H), 0.95 (s, 3H), 0.94 (s, 1H), 0.90 (d, *J* = 5.2 Hz, 18H), 0.15 (s, 3H), 0.06 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 210.62, 141.85, 120.21, 72.61, 72.50, 51.99, 49.12, 46.89, 46.78, 42.79, 37.28, 36.78, 33.50, 32.05, 31.38, 30.36, 29.90, 26.07, 19.50, 18.41, 18.28, 9.13, -4.14, -4.44, -4.46, -4.68.
FTIR (NaCl, thin film, cm^{-1}): 2929, 2855, 1755, 1747, 1733, 1470, 1462, 1362, 1250, 1092 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{31}H_{54}O_3Si_2Br$: 609.2795 $[M+H–H_2]^+$; found: 609.2778.
$[\alpha]_D^{21}$: –94° (*c* = 0.400, $CHCl_3$).

Preparation of unsaturated ketone S2:

A 1 L round-bottom flask with a stir bar was charged with α-bromo ketone **10** (27.3 g, 44.7 mmol), Li_2CO_3 (13.6 g, 224 mmol, 5.0 equiv), LiBr (14.6 g, 215 mmol, 4.8 equiv) and DMF (300 mL, 0.15 M). The resulting mixture was heated to 150 °C for 12 h. After cooling to room temperature, the reaction was filtered through a glass filter, washed with hexane (2 × 50 mL), the combined brown solution was diluted with hexane (100 mL) and H_2O (300 mL). The layers were separated. The aqueous layer was further extracted with hexane (3 × 150 mL), combined organic layers were washed with brine (2 × 150 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography (5 to 7.5 to 10% Et_2O/hexanes) to afford unsaturated ketone **S2** (19.0 g, 35.8 mmol, mixture of two regio isomers **S2a** ($\Delta^{14–15}$) and **S2b** ($\Delta^{15–16}$), **S2a**:**S2b** = 2.3:1, 80% yield) as a yellow foam. This mixture can be used directly in the next reaction, though it was purified further to obtain pure **S2a** for analytical characterization.

Pure **S2a**
TLC (8% Et_2O/hexanes): R_f = 0.26 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.97 (dd, *J* = 6.0, 3.1 Hz, 1H), 5.36 (m, 1H), 4.01 (dd, *J* = 10.1, 5.4 Hz, 1H), 3.48 (tt, *J* = 10.5, 4.7 Hz, 1H), 2.26 (m, 3H), 2.15 (ddd, *J* = 11.3, 3.1, 1.8 Hz, 1H), 1.80 (m, 1H), 1.76 (m, 3H), 1.72 – 1.66 (m, 1H), 1.60 – 1.56 (m, 2H), 1.54 – 1.52 (m, 1H), 1.25 (s, 1H), 1.09 (s, 3H), 1.07 (s, 3H), 0.92 (s, 9H), 0.89 (s, 9H), 0.16 (s, 3H), 0.06 (d, *J* = 0.8 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 210.60, 156.63, 142.29, 132.55, 119.87, 77.35, 77.03, 76.71, 72.39, 70.80, 55.18, 54.74, 50.71, 42.71, 37.07, 36.92, 31.91, 31.28, 30.38, 27.71, 25.94, 19.32, 18.28, 18.19, 15.10, -4.31, -4.57, -4.59, -4.75.
FTIR (NaCl, thin film, cm^{-1}): 2953, 2928, 2854, 1723, 1714, 1470, 1462, 1456, 1363, 1252, 1092 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{31}H_{55}O_3Si_2$: 531.3690 $[M+H]^+$; found: 531.3688.
$[\alpha]_D^{21}$: –116° (*c* = 0.267, $CHCl_3$).

Mixture **S2a**:**S2b** (1:1):
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.97 (dd, *J* = 5.9, 3.1 Hz, 1H), 5.60 (q, *J* = 2.2 Hz, 1H), 5.38 (ddt, *J* = 14.9, 3.5, 2.0 Hz, 2H), 4.01 (dd, *J* = 10.1, 5.4 Hz, 1H), 3.57 – 3.51 (m, 1H), 3.48 (tt, *J* = 10.5, 4.8 Hz, 2H), 2.95 – 2.78 (m, 2H), 2.33 – 2.27 (m, 2H), 2.25 (s, 1H), 2.23 (dd, *J* = 5.3, 1.9 Hz, 2H), 2.20 (dd, *J* = 5.4, 2.1 Hz, 1H), 2.17 (dd, *J* = 3.1, 1.9 Hz, 1H), 2.15 – 2.09 (m, 2H), 1.81 (d, *J* = 4.7 Hz, 1H), 1.80 – 1.73 (m, 5H), 1.67 (dt, *J* = 13.4, 5.0 Hz, 2H), 1.62 – 1.59 (m, 1H), 1.57 (td, *J* = 6.6, 6.2, 2.6 Hz, 2H), 1.53 (d, *J* = 3.0 Hz, 1H), 1.11 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H), 1.05 – 1.02 (m, 2H), 0.92 (s, 9H), 0.91 (s, 9H), 0.89 (s, 18H), 0.16 (s, 3H), 0.06 (s, 15H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 218.90, 210.71, 156.75, 151.57, 142.40, 140.98, 132.67, 120.49, 120.00, 116.41, 72.55, 72.51, 72.02, 70.91, 56.53, 55.29, 54.85, 50.82, 48.74, 42.83, 42.76, 41.75, 37.26, 37.18, 37.11, 37.03, 32.03, 31.40, 30.93, 30.85, 30.50, 27.86, 27.82, 26.07, 26.03, 19.45, 19.32, 18.41, 18.31, 18.28, 15.23, 13.54, -4.18, -4.32, -4.45, -4.46, -4.62, -4.75.

Preparation of TMS enol ether 11:

A 1 L round-bottom flask with a stir bar was charged with unsaturated ketone **S2** (16.7 g, 31.5 mmol, mixture of two regio isomers, **S2a**:**S2b** = 2.3:1), Et_3N (19.8 mL, 142 mmol, 4.5 equiv) and CH_2Cl_2 (315

mL, 0.1 M). TMSOTf (17.1 mL, 94.5 mmol, 3.0 equiv) was added to the reaction at room temperature. After stirring at room temperature for 30 min, the reaction was diluted with hexane (150 mL), quenched with H_2O (150 mL). The layers were separated. The aqueous layer was further extracted with hexane (3 × 150 mL), combined organic layers were washed with st. $NaHCO_3$ aq. (150 mL) and brine (2 × 150 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was dissolved in Et_2O (80 mL), and then MeCN (400 mL) was added. The resulting solid was collected by filtration, washed with MeCN (2 × 80 mL), dried under high vacuum to afford TMS enol ether **11** (17.2 g, 28.0 mmol, 89% yield) as a white solid.

TLC (2% Et_2O/hexanes): R_f = 0.38 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (t, *J* = 2.2 Hz, 1H), 5.40 (dt, *J* = 4.2, 2.0 Hz, 1H), 5.13 (d, *J* = 2.4 Hz, 1H), 3.48 (m, 1H), 3.19 (dd, *J* = 10.6, 4.7 Hz, 1H), 2.33 – 2.24 (m, 1H), 2.22 (m, 1H), 2.19 (m, 1H), 2.15 (m, 1H), 2.11 – 2.04 (m, 1H) 1.80 – 1.70 (m, 2H), 1.63 – 1.57 (m, 2H), 1.54 – 1.49 (m, 1H), 1.07 (s, 3H), 1.01 (s, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.86 – 0.80 (m, 1H), 0.22 (s, 9H), 0.06 (m, 7H), 0.02 (s, 3H), 0.01 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.35, 145.14, 140.92, 121.09, 119.48, 101.93, 76.31, 72.71, 56.13, 50.20, 42.83, 37.64, 37.11, 32.12, 31.76, 30.81, 28.49, 26.18, 26.09, 19.53, 18.42, 18.33, 12.39, 0.22, -4.42, -4.44, -4.53.
FTIR (NaCl, thin film, cm^{-1}): 2928, 2892, 2856, 1714, 1471, 1462, 1386, 1372, 1361, 1255, 1089 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{34}H_{62}O_3Si_3$: 602.4007 $[M+\bullet]^-$; found: 602.4002.
$[\alpha]_D^{21}$: +113° (*c* = 0.200, $CHCl_3$).

Preparation of α-hydroxy ketone 12:

A 4 L flask with a stir bar was charged with TMS enol ether **11** (17.2 g, 28.0 mmol), $Me_2C{=}CHMe$ (5.93 mL, 56.0 mmol, 2.0 equiv) and THF (1500 mL, 0.02 M). The solution was cooled to –78 °C and stirred at this temperature for 30 min. Thereafter, DMDO solution (0.060 M in acetone, 513 mL, 30.8 mmol, 1.1 equiv) was added dropwise by cannula. The reaction was stirred at –78 °C for 30 min, then warmed to room temperature. After stirring for 30 min, TBAF (1.0 M in THF, 28.0 mL, 28.0 mmol, 1.0 equiv) was added dropwise. After stirring for 30 min, the reaction was diluted with EtOAc (500 mL), quenched with H_2O (500 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 150 mL), combined organic layers were washed with brine (2 × 150 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography (5 to 7.5% EtOAc/hexanes) to afford α-hydroxy ketone **12** (14.1 g, 25.8 mmol, 92% yield) as a colorless foam.

Note: Compound **12** decomposes within hours at room temperature under air, and is stable for roughly two weeks at freezer temperature under inert atmosphere.

Preparation of DMDO solution in acetone: A three-necked 4 L flask was charged with $NaHCO_3$ (1.05 kg), acetone (1.1 L) and H_2O (1.7 L). The flask was fitted with a tall reflux condenser, which was connected to a distillation neck with a 1L receiving flask charged with activated 3Å MS pellets. The distillation neck was cooled with circulating ice water and the receiving flask was cooled in a dry ice/acetone bath. Oxone

(2.5 kg) was added in several portions over 15 min at room temperature, the resulting DMDO was carefully distilled directly from the reaction mixture over 30 min under low pressure using a diaphragm pump. The concentration of DMDO solution was ditermined by ^{1}H NMR using thioanisole.

TLC (15% EtOAc/hexanes): R_f = 0.41 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (t, *J* = 2.0 Hz, 1H), 5.39 (m, 1H), 4.76 (dd, *J* = 3.7, 1.9 Hz, 1H), 3.63 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.54 – 3.43 (m, 1H), 2.53 (s, 1H), 2.33 – 2.26 (m, 1H), 2.23 (m, 2H), 2.17 (m, 1H), 2.06 (m, 1H), 1.81 (dt, *J* = 12.7, 3.3 Hz, 1H), 1.75 (m, 1H), 1.69 (dt, *J* = 13.3, 4.2 Hz, 1H), 1.63 – 1.49 (m, 3H), 1.20 (s, 3H), 1.16 – 1.10 (m, 1H), 1.08 (m, 1H), 1.04 (m, 4H), 0.92 (s, 9H), 0.91 (s, 3H), 0.89 (s, 9H), 0.11 (s, 3H), 0.10 (s, 2H), 0.06 (s, 6H), 0.03 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 217.10, 154.88, 140.87, 121.40, 120.18, 77.45, 77.14, 76.82, 74.14, 72.43, 71.67, 54.43, 47.31, 42.69, 37.17, 36.90, 31.96, 30.84, 30.73, 27.91, 26.05, 26.01, 25.77, 19.24, 18.38, 18.22, 14.39, -3.46, -4.12, -4.47, -4.74.
FTIR (NaCl, thin film, cm^{-1}): 3410, 2929, 2888, 2857, 1759, 1471, 1462, 1371, 1360, 1252, 1096 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{31}H_{53}O_4Si_2$: 545.3482 $[M+H]^+$; found: 545.3461.
$[\alpha]_D^{21}$: –37° (*c* = 0.333, CH_2Cl_2).

2ii. Synthesis of western propargyl bromide 6

Preparation of PMP ether S3:

A 500 mL round-bottom flask with a stir bar was charged with *p*-methoxy phenol (20.0 g, 161 mmol), K_2CO_3 (24.5 g, 177 mmol, 1.1 equiv), KI (2.67 g, 16.1 mmol, 10 mol %), 2-methyl allylchloride (17.3 mL, 177 mmol, 1.1 equiv) and acetone (80 mL, 2.0 M). The resulting mixture was heated to 50 °C and stirred for 12 h. After cooling to room temperature, the solid was removed by filtration and washed with EtOAc (2 × 50 mL), the resulting solution was diluted with H_2O (100 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 50 mL), combined organic layers were washed with st. $Na_2S_2O_3$ aq. (50 mL) and brine (2 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (10 to 15% Et_2O/hexanes) to afford PMP ether **S3** (27.0 g, 151 mmol, 94% yield) as colorless crystals. Spectroscopic data were identical to those reported in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 – 6.79 (m, 4H), 5.09 (m, 1H), 4.98 (m, 1H), 4.39 (m, 2H), 3.77 (s, 3H), 1.83 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 153.95, 153.05, 141.35, 115.84, 114.68, 112.70, 72.55, 55.83, 19.56.

Preparation of diol S4:

A 1 L round-bottom flask with a stir bar was charged with AD-mix-β (70.0 g, 1.4 g/mmol), *t*-BuOH (230 mL, 0.1 M total) and H_2O (250 mL, 0.1 M total). The resulting mixture was stirred at room temperature until the solid was completely disolved. The reaction was cooled to 0°C and stirred at this temperature for 1 h. Thereafter, PMP ether **S3** (8.91 g, 50.0 mmol) was added, rinsed with *t*-BuOH (2 × 10 mL). The reaction was stirred at 0 °C for 24 h, quenched with Na_2SO_3 (75.0 g, 1.5 g/mmol), diluted with EtOAc (250

mL) and H_2O (120 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 150 mL), combined organic layers were washed with brine (2 × 150 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (65 to 100% EtOAc/hexanes) to afford diol **S4** (10.3 g, 48.6 mmol, 97% yield, 92% ee) as a white solid. Spectroscopic data were identical to those reported in the literature.[4]

TLC (50% EtOAc/hexanes): R_f = 0.21 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 – 6.79 (m, 4H), 3.94 – 3.83 (m, 2H), 3.77 (s, 3H), 3.65 (dd, *J* = 61.1, 11.2 Hz, 2H), 1.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.39, 152.75, 115.70, 114.84, 73.81, 72.11, 67.95, 55.88, 21.61.
FTIR (NaCl, thin film, cm^{-1}): 3342, 3303, 2923, 2836, 1513, 1470, 1291, 1243, 1148, 1051 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{11}H_{16}O_4$: 212.1049 [M+•]$^-$; found: 212.1022.
$[\alpha]_D^{21}$: +0.86° (*c* = 0.250, $CHCl_3$).

SFC data for racemic S4:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.915	BB	0.1947	2767.92993	207.42258	49.9694
2	5.570	BB	0.2228	2771.32056	182.88441	50.0306

SFC data for enantioenriched S4:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.925	BB	0.1562	180.82196	15.71460	4.2452
2	5.580	BB	0.1944	4078.62842	304.27750	95.7548

Preparation of epoxide (S5):

A 2 L round-bottom flask with a stir bar was charged with diol **S4** (10.3 g, 48.6 mmol) and THF (500 mL, 0.1 M). NaH (60% in mineral oil, 5.83 g, 146 mmol, 3.0 equiv) was added in one portion at room temperature. This was accompanied by a slight exotherm and formation of gas. After stirring for 1 h, TsCl (10.2 g, 53.5 mmol, 1.1 equiv) was added in one portion at room temperature. After stirring for 24 h at room temperature, the reaction was poured into an ice-cooled mixture of Et_2O (500 mL), st. NH_4Cl aq. (250 mL) and H_2O (250 mL). The layers were separated. The aqueous layer was further extracted with Et_2O (3 × 200 mL), combined organic layers were washed with brine (2 × 200 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (7 to 10% EtOAc/hexanes) to afford epoxide **S5** (9.15 g, 47.1 mmol, 97% yield) as a white solid.

TLC (50% EtOAc/hexanes): R_f = 0.66 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 – 6.77 (m, 4H), 4.00 – 3.88 (m, 2H), 3.77 (s, 3H), 2.79 (dd, *J* = 55.2, 4.8 Hz, 2H), 1.48 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.25, 152.97, 115.82, 114.76, 72.41, 55.85, 55.77, 52.19, 18.65.
FTIR (NaCl, thin film, cm^{-1}): 3047, 2994, 2934, 2834, 1513, 1505, 1455, 1290, 1234, 1037 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{11}H_{14}O_3$: 194.0943 $[M+\bullet]^-$; found: 194.0969.
$[\alpha]_D^{21}$: –12° (*c* = 0.150, $CHCl_3$).

Preparation of propargyl alcohol S6:

A 200 mL round-bottom flask with a stir bar was charged with (±)-3-butyn-2-ol (392 μL, 5.0 mmol, 2.0 equiv) and PhMe (25 mL, 0.1 M). The resulting solution was cooled to 0 °C and stirred at this temperature for 1 h. Thereafter, *n*-BuLi (2.5 M in hexane, 4.0 mL, 10 mmol, 4.0 equiv) was added dropwise at 0 °C. After stirring at 0 °C for 1 h, Et_2AlCl (25 wt. % in PhMe, 2.7 mL, 5.0 mmol, 2.0 equiv) was added dropwise. After stirring at 0 ° C for 1 h, epoxide **S5** (486 mg, 2.5 mmol) in PhMe (2.5 mL, rinsed with 2.5 mL) was added dropwise. The resulting mixture was stirred at room temperature for 18 h, then was diluted with Et_2O (20 mL), quenched with st. NH_4Cl aq. (10 mL), st. Na/K-tartrate aq. (10 mL) and H_2O (10 mL). After vigorously stirring for 1 h, the layers were separated. The aqueous layer was further extracted with Et_2O (3 × 20 mL), combined organic layers were washed with brine (2 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (50 to 75 to 100% EtOAc/hexanes) to afford propargyl alcohol **S6** (238 mg, 0.9 mmol, 1:1 mixture of diastereomers, 36% yield) as a colorless oil.

TLC (50% EtOAc/hexanes): R_f = 0.19 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 – 6.78 (m, 4H), 4.56 – 4.46 (m, 1H), 3.87 (dd, *J* = 8.9, 1.1 Hz, 1H), 3.84 – 3.80 (m, 1H), 3.77 (s, 3H), 2.63 – 2.52 (m, 3H), 2.51 – 2.24 (m, 1H), 1.42 (dd, *J* = 6.6, 0.8 Hz, 3H), 1.38 (d, *J* = 0.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.30, 152.86, 115.77, 114.81, 85.30, 80.30, 74.45, 71.64, 58.52, 55.87, 29.76, 24.69, 23.87.
FTIR (NaCl, thin film, cm^{-1}): 3390, 2978, 2933, 2249, 2064, 1732, 1504, 1470, 1228, 1049 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{15}H_{20}O_4$: 264.1362 [M+•]$^+$; found: 264.1368.
$[\alpha]_D^{20}$: +2.3° (c = 0.333, $CHCl_3$).

Preparation of propargyl bromide 6:

A 25 mL round-bottom flask was charged with propargyl alcohol **S6** (160 mg, 0.60 mmol), CBr_4 (358 mg, 1.08 mmol, 1.8 equiv), 2,6-lutidine (280 µL, 2.4 mmol, 4.0 equiv) and CH_2Cl_2 (3.0 mL, 0.2 M). Ph_3P (262 mg, 1.0 mmol, 1.65 equiv) was added in one portion at room temperature. After stirring for 30 min, TBSOTf (207 µL, 0.9 mmol, 1.5 equiv) was added. After stirring for 30 min at room temperature, the reaction was diluted with hexane (3 mL), quenched with H_2O (3 mL). The layers were separated. The aqueous layer was further extracted with hexane (3 × 3 mL), combined organic layers were washed with st. $Na_2S_2O_3$ aq. (2 × 5 mL), st. $NaHCO_3$ aq. (5 mL) and brine (2 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (0 to 5 to 10% Et_2O/hexanes) to afford propargyl bromide **6** (207 mg, 0.47 mmol, 1:1 mixture of diastereomers, 78% yield) as a colorless oil.

TLC (10% EtOAc/hexanes): R_f = 0.65 (p-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (m, 4H), 4.62 (m, 1H), 3.81 (dd, J = 8.9, 1.8 Hz, 1H), 3.77 (m, 4H), 2.60 (ddd, J = 16.6, 2.2, 1.5 Hz, 1H), 2.53 (dd, J = 16.6, 2.2 Hz, 1H), 1.87 (dd, J = 6.8, 0.6 Hz, 3H), 1.39 (d, J = 1.0 Hz, 3H), 0.87 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.04, 153.10, 115.61, 115.59, 114.79, 84.48, 82.60, 74.66, 74.62, 74.58, 55.90, 32.45, 31.02, 27.87, 25.92, 25.09, 18.36, -2.25.
FTIR (NaCl, thin film, cm^{-1}): 2953, 2930, 2857, 1510, 1463, 1287, 1231, 1168, 1062, 834 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{21}H_{33}BrO_3Si$: 440.1382 [M+•]$^+$; found: 440.1363.
$[\alpha]_D^{21}$: +10° (c = 0.100, $CHCl_3$).

2iii. Synthesis of eastern propargyl bromide 7

Preparation of propargyl alcohol S7:

A 1 L round-bottom flask with a stir bar was charged with (±)-3-butyn-2-ol (5.88 mL, 75.0 mmol, 2.0 equiv) and THF (375 mL, 0.1 M). The resulting solution was cooled to –78 °C and stirred at this temperature for 30 min. Thereafter, *n*-BuLi (2.5 M in hexane, 60 mL, 150 mmol, 4.0 equiv) was added via cannula and the resulting mixture was stirred at –78 °C for 5 min, warmed to room temperature, and stirred at this temperature for 30 min, then cooled back to –78 °C. After stirring at –78 ° C for 30 min, BF_3•OEt_2 (6.95 mL, 56.3 mmol, 1.5 equiv) was added dropwise, followed by isobutylene oxide (3.33 mL, 37.5 mmol). The reaction was stirred at –78 °C for 30 min, then warmed to room temperature. After stirring for 12 h, the reaction was diluted with Et_2O (150 mL), quenched with st. NH_4Cl aq. (150 mL) and H_2O (150 mL). The layers were separated. The aqueous layer was further extracted with Et_2O (10 × 200 mL), combined organic layers were washed with brine (2 × 200 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (50 to 75% EtOAc/hexanes) to afford propargyl alcohol **S7** (3.61 g, 25.4 mmol, 68% yield) as a colorless oil.

TLC (50% EtOAc/hexanes): R_f = 0.16 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.55 (qt, *J* = 6.7, 2.0 Hz, 1H), 2.40 (d, *J* = 1.9 Hz, 2H), 1.82 (s, 2H), 1.46 (dd, *J* = 6.5, 0.5 Hz, 3H), 1.31 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.42, 81.00, 70.21, 58.44, 34.33, 28.78, 24.72.
FTIR (NaCl, thin film, cm^{-1}): 3356, 2973, 2930, 2249, 1666, 1462, 1366, 1154, 1080, 1006 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_8H_{13}O$: 125.0966 $[M–H_2O]^+$; found: 125.0994.

Preparation of propargyl bromide 7:

A 500 mL round-bottom flask with a stir bar was charged with propargyl alcohol **S7** (2.93 g, 20.6 mmol), CBr_4 (12.3 g, 37.1 mmol, 1.8 equiv), 2,6-lutidine (9.60 mL, 82.4 mmol, 4.0 equiv) and CH_2Cl_2 (100 mL, 0.2 M). Ph_3P (8.92 g, 34.0 mmol, 1.65 equiv) was added in one portion at room temperature. After stirring

for 30 min, TMSOTf (5.59 mL, 30.9 mmol, 1.5 equiv) was added. After stirring for 30 min at room temperature, the reaction was diluted with hexane (100 mL), quenched with H_2O (100 mL). The layers were separated. The aqueous layer was further extracted with hexane (3 × 100 mL), combined organic layers were washed with st. $Na_2S_2O_3$ aq. (2 × 100 mL), st. $NaHCO_3$ aq. (100 mL) and brine (2 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (0 to 5 to 10% Et_2O/hexanes) to afford propargyl bromide **7** (4.84 g, 17.5 mmol, 85% yield) as a colorless oil.

TLC (10% EtOAc/hexanes): R_f = 0.75 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.65 (qt, *J* = 6.8, 2.2 Hz, 1H), 2.38 (d, *J* = 2.2 Hz, 2H), 1.90 (d, *J* = 6.8 Hz, 3H), 1.32 (s, 6H), 0.13 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 85.31, 82.32, 73.69, 35.49, 32.60, 29.56, 27.97, 2.64.
FTIR (NaCl, thin film, cm^{-1}): 2976, 2930, 2243, 1442, 1382, 1366, 1250, 1216, 1182, 1048 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_8H_{12}Br$: 187.0122 $[M–OTMS]^+$; found: 187.0142.

2iv. Synthesis of western azido ketone 18

Preparation of homopropargyl alcohol 13:

A 500 mL round-bottom flask with a stir bar was charged with α-hydroxy ketone **12** (3.45 g, 6.35 mmol, 1.0 equiv), western propargyl bromide **6** (5.59 g, 12.7 mmol, 2.0 equiv) and CH_2Cl_2 (125 mL, 0.05 M). The resulting solution was cooled to –78 °C and stirred at this temperature for 30 min. Thereafter, *n*-BuLi (2.5 M in hexane, 2.67 mL, 6.67 mmol, 1.05 equiv) was added dropwise at –78 °C. After stirring for 15 min, Ti(O*i*-Pr)$_4$ (3.76 mL, 12.7 mmol, 2.0 equiv) was added dropwise at –78 °C. After stirring for 15 min, *i*-PrMgCl (2.0 M in Et_2O, 12.7 mL, 25.4 mmol, 4.0 equiv) was added dropwise at –78 °C. The reaction was stirred at –78 °C for 30 min, then warmed to room temperature. After stirring at room temperature for 12 h, the reaction was diluted with Et_2O (100 mL), quenched with st. NH_4Cl aq. (100 mL) and H_2O (100 mL). After vigorously stirring for 3 h, the resulting solid was removed by filtration, washed with Et_2O (2 × 100 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 100 mL), combined organic layers were washed with brine (2 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (10 to 15 to 20% EtOAc/hexanes) to afford homopropargyl alcohol **13** (3.12 g, 3.43 mmol, 1:1 mixture of diastereomers at C20′, 54% yield) as a colorless foam.

TLC (15% EtOAc/hexanes): R_f = 0.26 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (m, 8H), 5.38 – 5.32 (m, 2H), 5.26 (m, 1H), 5.13 (t, *J* = 1.8 Hz, 1H), 4.87 (s, 1H), 4.71 (s, 1H), 4.23 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.17 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.84 – 3.79 (m, 3H), 3.76 (t, *J* = 1.5 Hz, 8H), 3.65 (d, *J* = 3.3 Hz, 1H), 3.50 – 3.42 (m, 2H), 3.26 (s, 1H), 3.12 (qt, *J* = 7.1, 2.3 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.56 (ddd, *J* = 20.0, 16.3, 2.2 Hz, 4H), 2.44 (dt, *J* = 16.4, 2.5 Hz, 2H), 2.31 – 2.19 (m, 6H), 2.12 – 2.03 (m, 3H), 2.00 (m, 1H), 1.97 – 1.95 (m, 1H), 1.94 – 1.87 (m, 1H), 1.80 – 1.70 (m, 6H), 1.67 (m, 2H), 1.61 – 1.47 (m, 8H), 1.36 (d, *J* = 4.2 Hz, 6H), 1.31 (s, 2H), 1.30 – 1.28 (m, 4H), 1.27 – 1.25 (m, 4H), 1.12 (s, 1H), 1.09 (d, *J* = 2.1 Hz, 6H), 1.06 (m, 2H), 1.05 – 1.03 (m, 2H), 1.02 (s, 1H), 1.00 (d, *J* = 3.8 Hz, 6H), 0.97 (s, 1H), 0.93 (s, 3H), 0.92 (d, *J* = 2.5 Hz, 3H), 0.89 (m, 36H), 0.86 (d, *J* = 3.3 Hz, 18H), 0.11 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.08 (s, 3H), 0.07 (s, 4H), 0.06 (s, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.23, 153.97, 153.91, 153.63, 153.21, 153.16, 140.70, 140.68, 122.95, 121.95, 120.82, 115.51, 115.48, 114.74, 114.72, 86.26, 84.22, 82.46, 82.35, 80.77, 79.42, 78.78, 76.75, 74.79, 74.75, 74.57, 74.38, 73.35, 72.56, 72.43, 57.94, 56.87, 55.86, 55.82, 47.83, 47.48, 42.73, 37.10, 37.01, 34.28, 33.81, 32.91, 32.08, 31.03, 30.63, 30.24, 30.18, 30.07, 29.85, 29.21, 28.97, 26.24, 26.17, 26.08, 25.92, 25.19, 25.05, 22.49, 19.30, 19.28, 18.96, 18.41, 18.33, 18.32, 18.25, 17.62, 14.80, 14.42, 14.22, -2.20, -2.21, -2.26, -3.34, -3.52, -3.57, -3.76, -4.43.
FTIR (NaCl, thin film, cm^{-1}): 3500, 2948, 2928, 2854, 1723, 1715, 1506, 1462, 1372, 1230, 1090 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{52}H_{87}O_7Si_3$: 907.5760 $[M+H–H_2]^+$; found: 907.5748.
$[\alpha]_D^{21}$: –68° (*c* = 0.200, $CHCl_3$).

Preparation of α-hydroxy enone S8:

A 500 mL round-bottom flask with a stir bar was charged with homopropargyl alcohol **13** (3.00 g, 3.30 mmol, 1:1 mixture of diastereomers at C20′), $Cu(MeCN)_4OTf$ (123 mg, 0.33 mmol, 10 mol %), ^{MeO}bpy (mg, 0.33 mmol, 10 mol %), ABNO (71.4 mg, 0.33 mmol, 10 mol %), NMI (52.6 µL, 0.66 mmol, 20 mol %) and MeCN/THF (3:1, 330 mL, 0.01 M). The resulting solution was sparged with O_2 for 5 min, then vigurously stirred (1200 rpm) at room temperature under O_2 atmosphere for 12 h. The reaction was passed through a short pad of SiO_2 using 50% EtOAc/hexanes as the eluent and concentrated in vacuo. The crude product was purified by flash column chromatography (15 to 20 to 25% EtOAc/hexanes) to afford α-hydroxy enone **S8** (2.81 g, 3.10 mmol, 1:1 mixture of diastereomers at C20′, 94% yield) as a colorless foam.

TLC (15% EtOAc/hexanes): R_f = 0.31 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 – 6.80 (m, 8H), 5.83 (dd, *J* = 22.2, 1.5 Hz, 2H), 5.34 (m, 2H), 3.92 – 3.86 (m, 2H), 3.76 (s, 6H), 3.74 (d, *J* = 3.8 Hz, 2H), 3.72 (s, 1H), 3.71 (s, 1H), 3.49 (dd, *J* = 10.5, 5.2 Hz, 2H), 3.43 (d, *J* = 15.9 Hz, 2H), 3.01 – 2.91 (m, 1H), 2.74 (m, 1H), 2.51 (ddd, *J* = 16.2, 12.9, 2.2 Hz, 3H), 2.41 – 2.30 (m, 4H), 2.30 – 2.18 (m, 6H), 2.04 – 1.93 (m, 4H), 1.80 – 1.70 (m, 8H), 1.69 – 1.64 (m, 2H), 1.64 – 1.59 (m, 2H), 1.58 – 1.52 (m, 2H), 1.42 (s, 3H), 1.39 (s, 3H), 1.35 (m, 4H), 1.31 (s, 3H), 1.29 (s, 1H), 1.28 (s, 3H), 1.27 (s, 1H), 1.11 (d, *J* = 10.8 Hz, 2H), 1.08 (d, *J* = 2.0 Hz, 1H), 1.06 (s, 3H), 1.05 (s, 4H), 1.03 (d, *J* = 5.9 Hz, 2H), 1.00 (d, *J* = 3.0 Hz, 1H), 0.98 (d, *J* = 4.1 Hz, 1H), 0.94 (d, *J* = 2.1 Hz, 1H), 0.93 (d, *J* = 1.4 Hz, 2H), 0.92 (s, 1H), 0.91 (s, 2H), 0.90 (s, 6H), 0.89 (s, 15H), 0.89 (s, 3H), 0.88 (s, 8H), 0.86 (m, 4H), 0.83 (s, 6H), 0.83 (s, 8H), 0.08 (s, 6H), 0.07 (s, 3H), 0.06 (s, 15H), 0.06 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 206.72, 186.78, 185.46, 153.87, 153.10, 140.80, 140.72, 125.28, 124.93, 120.12, 120.07, 115.47, 115.33, 114.77, 114.74, 114.72, 84.18, 83.05, 82.55, 82.47, 81.50, 81.20, 76.52, 75.58, 74.75, 74.69, 74.12, 74.04, 72.31, 55.99, 55.80, 55.02, 48.42, 48.15, 47.79, 42.66, 37.73, 37.21, 33.38, 32.69, 32.17, 32.02, 31.98, 30.95, 30.88, 30.27, 30.03, 28.43, 28.13, 26.06, 26.03, 25.93, 25.89, 24.98, 19.38, 19.32, 18.40, 18.32, 18.28, 18.24, 18.19, 16.28, 15.78, 13.21, 12.09, -2.31, -2.92, -3.19, -4.16, -4.45, -4.47.
FTIR (NaCl, thin film, cm^{-1}): 3467, 2953, 2931, 2856, 1704, 1608, 1507, 1463, 1372, 1231, 1092 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{52}H_{85}O_7Si_3$: 905.5603 $[M+H–H_2]^+$; found: 905.5611.
$[\alpha]_D^{21}$: +57° (*c* = 0.133, $CHCl_3$).

Preparation of primary alcohol S9:

A 500 mL round-bottom flask with a stir bar was charged with α-hydroxy enone **S8** (3.81 g, 4.21 mmol, 1:1 mixture of diastereomers at C20′) and MeCN/THF/H_2O (2:2:1, 135 mL, 0.03 M). The resulting solution was cooled to 0 °C and stirred at this temperature for 15 min. Thereafter, $Ag(DPAH)_2$•H_2O (7.38 g, 16.8 mmol, 4.0 equiv) was added in one portion. After stirring for 30 min at 0 °C, the reaction was warmed to

room temperature stirred for 1 h, then diluted with EtOAc (100 mL), quenched with st. $Na_2S_2O_3$ aq. (100 mL) and H_2O (100 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 100 mL), combined organic layers were washed with brine (2 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (10 to 15 to 20% EtOAc/hexanes) to afford primary alcohol **S9** (2.46 g, 3.07 mmol, 1:1 mixture of diastereomers at C20′, 73% yield) as a colorless foam.

Preparation of $Ag(DPAH)_2$•H_2O: A 2 L round-bottom flask with a stir bar was charged with $AgNO_3$ (3.0 g, 17.4 mmol), 2,6-pyridinedicarboxylic acid (4.28 g, 34.8 mmol, 2.0 equiv) and H_2O (870 mL, 0.02 M). $K_2S_2O_8$ (23.5 g, 87.1 mmol, 5.0 equiv) was added in one portion and the resulting solution was stirred at room temperature for 24 h. The resulting solid was collected by filtration, washed with H_2O (2 × 50 mL), dried under high vacuum to afford $Ag(DPAH)_2$•H_2O (6.79 g, 15.5 mmol, 89% yield) as a black solid.[5]

TLC (20% EtOAc/hexanes): R_f = 0.46 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (dd, *J* = 9.4, 1.5 Hz, 2H), 5.40 (dd, *J* = 5.1, 2.3 Hz, 2H), 3.94 (dd, *J* = 11.0, 5.0 Hz, 2H), 3.49 (m, 4H), 3.46 – 3.39 (m, 2H), 3.33 (dd, *J* = 13.2, 10.6 Hz, 2H), 2.96 (qt, *J* = 7.1, 2.4 Hz, 1H), 2.75 (qt, *J* = 7.1, 2.3 Hz, 1H), 2.60 – 2.49 (m, 2H), 2.44 (ddd, *J* = 18.4, 16.2, 2.2 Hz, 2H), 2.30 (dd, *J* = 13.1, 2.6 Hz, 2H), 2.26 (s, 1H), 2.25 – 2.22 (m, 2H), 2.21 – 2.16 (m, 2H), 2.15 (d, *J* = 2.8 Hz, 1H), 2.13 – 2.07 (m, 1H), 1.84 – 1.79 (m, 2H), 1.77 (m, 3H), 1.74 (s, 3H), 1.70 (d, *J* = 12.7 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.47 (s, 2H), 1.45 (s, 3H), 1.37 (d, *J* = 7.0 Hz, 3H), 1.29 (d, *J* = 6.2 Hz, 4H), 1.25 (d, *J* = 5.1 Hz, 5H), 1.21 – 1.20 (m, 3H), 1.16 (dd, *J* = 11.8, 6.7 Hz, 2H), 1.12 (s, 3H), 1.11 (s, 3H), 1.10 – 1.06 (m, 2H), 1.06 – 0.98 (m, 2H), 0.93 (d, *J* = 4.7 Hz, 1H), 0.91 (s, 6H), 0.89 (d, *J* = 0.9 Hz, 24H), 0.86 (m, 3H), 0.85 (s, 6H), 0.85 (s, 7H), 0.10 (m, 6H), 0.09 (m, 9H), 0.07 (s, 3H), 0.06 (s, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 206.69, 206.65, 140.94, 140.89, 125.41, 125.38, 124.98, 124.97, 120.08, 120.03, 84.41, 82.51, 81.04, 76.53, 76.06, 76.02, 72.31, 72.30, 69.73, 69.59, 55.94, 55.08, 48.47, 48.19, 42.66, 37.80, 37.78, 37.22, 37.20, 33.42, 33.36, 33.28, 33.11, 33.01, 32.69, 32.32, 32.13, 32.03, 30.32, 30.11, 29.96, 29.86, 28.52, 28.24, 26.08, 26.06, 26.03, 25.88, 23.97, 23.93, 19.49, 18.40, 18.26, 18.21, 18.19, 15.79, 13.30, 12.18, -2.09, -2.12, -2.91, -3.22, -4.15, -4.42, -4.47.
FTIR (NaCl, thin film, cm^{-1}): 3470, 2951, 2930, 2856, 1704, 1608, 1472. 1462, 1254, 1092 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{45}H_{81}O_6Si_3$: 801.5341 $[M+H]^+$; found: 801.5359.
$[\alpha]_D^{21}$: +29° (*c* = 0.208, $CHCl_3$).

Preparation of allylic alcohol 4:

A 2 L round-bottom flask with a stir bar was charged with $NaBH_4$ (8.70 g, 230 mmol, 100 equiv) and THF (460 mL, 0.005 M). The resulting mixture was cooled to 0 °C and stirred at this temperature for 15 min. Thereafter, AcOH (52.5 mL, 0.92 mol, 400 equiv) was added dropwise at 0 °C, then warmed to room temperature. This was accompanied by a slight exotherm and formation of gas. The remaining AcOH (52.5 mL, 0.92 mol, 400 equiv) was then added. After stirring for 30 min at room temperature, primary alcohol **S9** (1.84 g, 2.30 mmol, 1.0 equiv) in THF (20 mL, further rinsed with 2 × 5.0 mL) was added. After stirring for 12 h at room temperature, the reaction was quenched with st. $NaHCO_3$ aq. (200 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 200 mL), combined organic layers were washed with brine (2 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude

product was purified by flash column chromatography (20 to 25 to 30% EtOAc/hexanes) to afford allylic alcohol **4** (1.59 g, 1.98 mmol, 1:1 mixture of diastereomers at C20′, 86% yield) as a colorless foam.

TLC (20% EtOAc/hexanes): R_f = 0.25 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.45 (t, *J* = 2.4 Hz, 1H), 5.42 (t, *J* = 2.2 Hz, 1H), 5.37 (m, 2H), 4.57 (m, 1H), 4.34 (d, *J* = 2.8 Hz, 1H), 4.05 (ddd, *J* = 11.6, 5.9, 4.2 Hz, 2H), 3.68 – 3.57 (m, 1H), 3.55 (d, *J* = 10.8 Hz, 1H), 3.51 (d, *J* = 10.7 Hz, 1H), 3.49 – 3.45 (m, 2H), 3.45 – 3.39 (m, 2H), 3.14 (qt, *J* = 7.0, 2.4 Hz, 1H), 3.04 (qt, *J* = 7.1, 2.0 Hz, 1H), 2.53 (dd, *J* = 11.1, 2.3 Hz, 1H), 2.49 (dd, *J* = 11.0, 2.3 Hz, 1H), 2.39 (dd, *J* = 16.3, 2.2 Hz, 1H), 2.33 (dd, *J* = 16.3, 2.3 Hz, 1H), 2.29 – 2.24 (m, 2H), 2.24 – 2.19 (m, 4H), 2.18 – 2.14 (m, 2H), 2.12 – 2.08 (m, 1H), 2.06 – 1.92 (m, 4H), 1.76 (m, 4H), 1.72 (d, *J* = 4.5 Hz, 2H), 1.70 (t, *J* = 4.5 Hz, 1H), 1.62 (d, *J* = 12.4 Hz, 1H), 1.58 (m, 1H), 1.57 (m, 1H), 1.55 – 1.49 (m, 2H), 1.40 (d, *J* = 7.1 Hz, 3H), 1.35 (d, *J* = 7.1 Hz, 3H), 1.31 (d, *J* = 3.0 Hz, 6H), 1.29 (s, 3H), 1.25 (s, 6H), 1.10 (s, 3H), 1.06 (d, *J* = 3.9 Hz, 1H), 1.05 (s, 3H), 1.03 (s, 1H), 1.01 (m, 4H), 0.92 (s, 1H), 0.92 (s, 6H), 0.91 (s, 9H), 0.90 (m, 2H), 0.89 (s, 15H), 0.88 (s, 2H), 0.87 (s, 9H), 0.87 (s, 1H), 0.86 (s, 6H), 0.85 (s, 1H), 0.14 (s, 3H), 0.13 (s, 3H), 0.12 (d, *J* = 1.4 Hz, 5H), 0.11 (d, *J* = 1.7 Hz, 5H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.37, 154.51, 140.71, 140.60, 122.74, 120.91, 120.78, 86.16, 86.04, 85.92, 85.58, 85.41, 85.14, 79.80, 79.19, 76.04, 75.85, 74.92, 72.53, 72.14, 70.03, 57.47, 57.36, 48.95, 47.59, 42.66, 37.28, 36.94, 32.73, 32.10, 31.07, 30.83, 30.53, 30.31, 30.24, 30.06, 29.85, 29.54, 28.81, 26.45, 26.22, 26.08, 25.91, 24.32, 24.17, 22.85, 22.49, 19.39, 19.32, 18.60, 18.41, 18.34, 18.23, 17.10, 15.89, 14.93, 1.17, -2.07, -2.43, -3.13, -3.70, -4.44.
FTIR (NaCl, thin film, cm^{-1}): 3437, 2957, 2927, 2854, 1471, 1463, 1372, 1256, 1090 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{45}H_{81}O_6Si_3$: 801.5341 $[M+H–H_2]^+$; found: 801.5333.
$[\alpha]_D^{21}$: –9.3° (*c* = 0.125, $CHCl_3$).

Preparation of spiroketal 15:

In an N_2-filled glovebox, a 100 mL round-bottom flask with a stir bar was charged with ^{Cy}JohnPhos•AuCl (36.7 mg, 0.06 mmol, 10 mol %), $AgBF_4$ (6.13 mg, 0.03 mmol, 5.0 mol %) and $(CH_2Cl)_2$ (21 mL, 0.03 M). The flask was removed from the glovebox and stirred at room temperature for 10 min. Allylic alcohol **4** (503 mg, 0.63 mmol, 1.0 equiv) in $(CH_2Cl)_2$ (2 mL, rinsed with 2 × 1.0 mL) was added. After stirring for 20 h, the reaction was passed through a short pad of SiO_2 using 20% EtOAc/hexanes as the eluent and concentrated in vacuo. The crude product was purified by flash column chromatography (0 to 5 to 10% EtOAc/hexanes) to afford spiroketal **15** (344 mg, 0.43 mmol, 68% yield) as a colorless foam.

TLC (8% EtOAc/hexanes): R_f = 0.44 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (t, *J* = 1.9 Hz, 1H), 5.37 (m, 1H), 4.64 (d, *J* = 2.3 Hz, 1H), 4.08 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.66 (d, *J* = 11.6 Hz, 1H), 3.52 – 3.42 (m, 2H), 3.22 (s, 1H), 2.31 – 2.19 (m, 2H), 2.15 (dd, *J* = 13.5, 4.7 Hz, 1H), 2.10 – 2.04 (m, 2H), 1.99 (q, *J* = 6.9 Hz, 1H), 1.81 (ddd, *J* = 11.8, 9.6, 4.0 Hz, 2H), 1.77 – 1.71 (m, 2H), 1.64 – 1.60 (m, 1H), 1.59 (d, *J* = 3.0 Hz, 1H), 1.54 (m, 2H), 1.33 (m, 1H), 1.25 (s, 2H), 1.12 (s, 3H), 1.08 (s, 3H), 1.06 (s, 1H), 1.05 (s, 3H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.91 (s, 6H), 0.89 (s, 9H), 0.88 (s, 6H), 0.10 (s, 9H), 0.08 (s, 3H), 0.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.72, 140.58, 120.91, 119.70, 107.28, 92.95, 91.64, 74.95, 72.53, 69.85, 69.38, 56.63, 48.88, 48.37, 42.73, 37.36, 37.31, 34.10, 32.11, 30.98, 30.42, 29.86, 28.65, 28.01, 26.57, 26.18, 26.07, 26.00, 19.48, 18.41, 18.34, 18.27, 14.88, 8.06, -2.04, -2.19, -2.77, -4.05, -4.45.
FTIR (NaCl, thin film, cm^{-1}): 3532, 2953, 2931, 2857, 1471, 1462, 1366, 1252, 1089, 1059 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{45}H_{81}O_6Si_3$: 801.5341 $[M+H–H_2]^+$; found: 801.5351.
$[\alpha]_D^{21}$: –104° (c = 0.133, $CHCl_3$).

Table S1. Optimization studies for western spiroketalization

entry	cat.	X	MY	Z	solvent	20′S/22′S (**15**)	20′R/22′S	20′S22′R	20′R/22′R
1	$PdCl_2(PhCN)_2$	10	–	–	MeCN/THF	33%	–	–	–
2	$PtCl_2$	10	–	–	DCE	37%	–	17%	–
3	$[Pt(C_2H_4)Cl_2]_2$	10	–	–	DCE	44%[a]	–	12%[a]	–
4	$HgCl_2$	10	–	–	DCE	–	6%	–	38%
5	$Ph_3PAuNTf_2$	10	–	–	DCE	41%	20%	5%	3%
6	AuCl	20	–	–	DCE	62%	–	–	–
7	AuCl	10	–	–	DCE	45%	–	–	–
8	AuCl	10	–	–	PhMe	27%	–	–	–
9	AuCl	10	–	–	THF	–	–	–	–
10	AuCl	10	–	–	Et_2O	4%	–	–	–
11	AuCl	5	–	–	DCE	52%	–	–	–
12	JohnPhos·Au(MeCN)SbF_6	10	–	–	DCE	46%	19%	–	–
13	JohnPhos·AuCl	10	–	–	DCE	10%	–	7%	–
15	JohnPhos·AuCl	10	–	–	MeOH	20%	2%	9%	–
16	JohnPhos·AuCl	10	AgOTf	10	DCE	44%[a]	–	22%[a]	–
17	–	–	AgOTf	10	DCE	25%[a]	–	14%[a]	–
18	JohnPhos·AuCl	10	$AgSbF_6$	10	DCE	44%[a]	–	11%[a]	–
19	JohnPhos·AuCl	10	$AgPF_6$	10	DCE	52%[a]	–	4%[a]	–
20	JohnPhos·AuCl	10	$AgBF_4$	10	DCE	58%[a]	–	–	–
21	JohnPhos·AuCl	10	$AgBF_4$	10	DCE	58%[a]	–	–	–
22	JohnPhos·AuCl	10	$AgNTf_2$	10	DCE	32%[a]	10%[a]	–	–
23	JohnPhos·AuCl	10	$AgNTf_2$	10	THF	40%	10%	–	–
24	JohnPhos·AuCl	20	$AgBF_4$	10	DCE	76%	5%	2%	–
25	JohnPhos·AuCl	10	$AgBF_4$	20	DCE	77%[b]	–	–	–
26	^{Cy}JohnPhos·AuCl	20	$AgBF_4$	10	DCE	63%	3%	–	–
27	IPr·AuCl	20	$AgBF_4$	10	DCE	56%	4%	–	–
28	PMe_3·AuCl	20	$AgBF_4$	10	DCE	44%	6%	–	–
29	PPh_3·AuCl	20	$AgBF_4$	10	DCE	54%	5%	–	–
30	^{Cy}JohnPhos·AuCl	10	$AgBF_4$	5	DCE	72%[c]	–	–	–

[a]C12′–OTBS deprotected. [b]Mix of 64% desired with 13% C12′–OH. [c]Isolated yield.

Minimized Structures and energies:

15

Single-point energy = -3082.95785963937 (Hartree)

N_atoms = 136

C	0.200633	-3.678912	-0.916686
C	0.347653	-2.467007	-1.7092325
C	0.744005	-1.267871	-0.9148065
O	1.5687955	-1.6099555	0.111838
C	1.5381655	-0.4872035	-1.886369
C	0.8853585	0.7681405	-2.004716
C	-0.134173	0.8741265	-1.245642
C	-0.9347195	2.041061	-1.0049915
C	-0.550866	3.188451	-1.822703
C	-1.1196715	4.4141595	-1.3622155
C	-1.67093	4.5922305	-0.226109
C	-2.2308525	5.874307	0.1204845
C	-1.7521545	6.378206	1.407227
O	-2.416175	7.5396265	1.654909
Si	-2.193256	8.7149525	2.7194515
C	-3.369792	9.9550165	2.1758225
C	-2.631524	8.1980255	4.3891065
C	-0.4794105	9.37401	2.6830895
C	-0.057511	9.6060135	1.294181
C	-0.4485845	10.654676	3.4086925
C	0.469698	8.452965	3.326004
C	-1.9678685	5.3743205	2.441396
C	-1.341937	4.1015075	2.083451
C	-1.7745335	3.5379695	0.7786155
C	-3.1834765	3.1043705	0.870883
C	-0.8667405	2.4006145	0.4323645
C	-1.0451705	1.224704	1.2984455
C	-0.1742205	0.102592	0.953563
O	-0.400336	-0.9649555	1.798664
Si	0.177218	-1.186496	3.293762
C	1.1767455	-2.6812695	3.24448
C	1.2268975	0.1815935	3.8051045
C	-1.252707	-1.4177875	4.411917
C	-2.0527165	-0.1888605	4.4947045
C	-2.104404	-2.503452	3.9038915
C	-0.780117	-1.7663525	5.7611415
C	-0.3693745	-0.326353	-0.4546535
C	-1.7270495	-0.856267	-0.643668
O	1.516954	-1.172041	-3.082208
C	1.3343405	-2.4801045	-2.8226925
C	0.8965635	-3.0758575	-4.089428
C	1.2034795	-4.495635	-4.2434435
C	2.59362	-4.8038815	-3.899427
C	3.535642	-4.226312	-4.8495825
O	2.6738015	-6.169178	-3.84323
Si	3.828751	-7.2610465	-4.020438
C	4.356791	-7.3882135	-5.7379445
C	5.267732	-6.892519	-2.999212
C	3.021351	-8.80666	-3.4727875
C	3.963562	-9.9316975	-3.5671195

C	2.5736185	-8.6699195	-2.079305
C	1.8533555	-9.0907495	-4.319063
C	2.8174555	-4.2870855	-2.544209
O	2.5707185	-2.9522485	-2.4396645
H	-0.0354685	-4.4973335	-1.513305
H	-0.5695395	-3.571889	-0.223601
H	1.0722335	-3.8867675	-0.3939465
H	-0.559616	-2.273429	-2.1785325
H	1.0068005	-1.8650735	0.8023455
H	2.5260005	-0.4096075	-1.558762
H	1.241538	1.502042	-2.635373
H	-1.930436	1.8075585	-1.224319
H	-0.817191	3.0215385	-2.818541
H	0.4915975	3.281152	-1.8277885
H	-1.0611125	5.2165375	-2.0159165
H	-2.023655	6.571328	-0.6241065
H	-3.272348	5.8190685	0.1924215
H	-0.7249965	6.5667295	1.3288665
H	-3.112518	10.351381	1.248626
H	-3.4442735	10.743417	2.851786
H	-4.3149545	9.5286735	2.0816825
H	-2.0016375	7.4622235	4.769072
H	-2.597849	9.00649	5.0460905
H	-3.60241	7.821631	4.407674
H	-0.688731	10.2731345	0.802365
H	0.904936	10.012401	1.2670285
H	-0.0419655	8.7245005	0.7411235
H	-0.745387	10.552656	4.4027465
H	0.521309	11.0437835	3.417937
H	-1.063108	11.3685295	2.965006
H	0.222798	8.2671035	4.320774
H	1.432421	8.8599195	3.319292
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H	-1.525696	3.409129	2.8399645
H	-0.3068075	4.2388395	2.052043
H	-3.486621	2.6110635	0.006342
H	-3.8195895	3.9164865	0.993063
H	-3.3384915	2.470823	1.681554
H	0.108519	2.7465865	0.5895225
H	-2.031601	0.897339	1.276368
H	-0.8504935	1.4908785	2.2850325
H	0.8192595	0.4012695	1.0488865
H	2.004668	-2.559225	2.624193
H	1.533895	-2.924774	4.1921985
H	0.637573	-3.499436	2.8930565
H	0.714481	1.080494	3.9113595
H	1.667517	-0.0369235	4.7235845
H	1.999328	0.3327775	3.123251
H	-2.4198215	0.0961915	3.56365

H -1.5063225 0.6096635 4.8824725
H -2.8752985 -0.330423 5.1234745
H -1.5946035 -3.410834 3.8564485
H -2.4663005 -2.292582 2.9509405
H -2.927649 -2.644344 4.5317575
H -0.246348 -2.660652 5.7736295
H -1.5923365 -1.884892 6.40739
H -0.1712025 -1.025016 6.1684595
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H -2.4498455 -0.174448 -0.3416375
H -1.8678045 -1.721456 -0.0866115
H -0.125357 -2.9141755 -4.209206
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H 0.5990975 -5.075383 -3.6231865
H 3.4966585 -3.1888485 -4.808089
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H 3.5492735 -7.5373515 -6.3775105
H 4.8490335 -6.5256285 -6.0484215
H 5.0117955 -6.7852515 -1.9960325
H 5.736298 -6.012381 -3.299708
H 5.9756795 -7.6545725 -3.064279
H 4.299072 -10.0831905 -4.541992
H 4.8005445 -9.798429 -2.960506
H 3.5025625 -10.817981 -3.2607675
H 3.371185 -8.5100575 -1.427831
H 2.08862 -9.540556 -1.76464
H 1.9085715 -7.877375 -1.970667
H 1.3763895 -9.9628125 -3.996303
H 1.1579775 -8.317215 -4.2863815
H 2.1195475 -9.236512 -5.316067
H 2.2319535 -4.8481715 -1.8880245
H 3.8131925 -4.3983815 -2.2613525

23

Single-point energy = -3082.954550249199 (Hartree)
N_atoms = 136
C 1.466518 -0.078627 2.535555
C 2.19979 0.4857655 1.405724
C 1.4772195 0.747566 0.120291
O 1.0333855 2.04133 0.071605
C 2.5366685 0.52288 -0.8813455
C 1.87228 0.078004 -2.0502105
C 0.6605685 -0.2386645 -1.810049
C -0.3076485 -0.7350785 -2.7491685
C 0.1198105 -0.572783 -4.137453
C -0.9352625 -0.8010155 -5.0716795

C	-2.1752095	-0.8755835	-4.782652
C	-3.1507085	-1.1325815	-5.8131405
C	-4.230389	-0.1455775	-5.8201545
O	-5.1781105	-0.5116205	-6.7324445
Si	-5.592588	0.327334	-8.034784
C	-6.0891305	1.9976615	-7.577062
C	-4.2013805	0.4443155	-9.17241
C	-6.9787615	-0.623924	-8.739758
C	-8.0743475	-0.6941745	-7.7616195
C	-6.5346625	-1.9900345	-9.053416
C	-7.466618	0.020027	-9.9683845
C	-4.8314535	-0.0606015	-4.498142
C	-3.8303275	0.2426255	-3.47692
C	-2.6845885	-0.7034435	-3.425315
C	-3.142154	-2.0116545	-2.9157065
C	-1.6312605	-0.112882	-2.542791
C	-1.9893465	-0.106712	-1.120438
C	-0.991572	0.5602855	-0.284477
O	-1.4266855	0.5698545	1.012926
Si	-2.170915	1.781596	1.7639375
C	-0.973065	2.7680325	2.67507
C	-2.9941975	2.8743405	0.5907905
C	-3.367006	0.976803	2.8887475
C	-4.3861205	0.258627	2.110545
C	-4.026739	1.9862645	3.7294495
C	-2.665452	0.0140755	3.749849
C	0.326677	-0.103918	-0.3896065
C	0.2814815	-1.455387	0.1937305
O	3.3212245	-0.469598	-0.331235
C	3.472911	-0.18686	0.97625
C	3.8981425	-1.424368	1.6220795
C	4.5598235	-1.233146	2.9146775
C	5.5931785	-0.1905565	2.877388
C	6.772911	-0.59721	2.1235295
O	5.8999815	0.197467	4.1530365
Si	6.876111	-0.3632395	5.291283
C	6.73248	-2.147931	5.497326
C	8.597207	0.032705	4.93857
C	6.3021925	0.5145445	6.78837
C	6.4673835	1.964903	6.613335
C	7.074198	0.081323	7.9625975
C	4.879162	0.2255335	7.018542
C	4.9878265	0.997386	2.262963
O	4.510152	0.734011	1.0198685
H	1.947742	0.1491135	3.429675
H	1.3654005	-1.109448	2.4887865
H	0.512841	0.328653	2.571502
H	2.487029	1.4417225	1.7058585
H	1.7762115	2.5801855	0.1766575
H	3.1251815	1.3767525	-1.024033
H	2.344166	0.024001	-2.9649205

H	-0.417811	-1.761423	-2.57171
H	0.499697	0.3934815	-4.274068
H	0.9178055	-1.213964	-4.3438245
H	-0.648425	-0.9095705	-6.062091
H	-2.6888345	-1.15926	-6.7458725
H	-3.6017495	-2.0656125	-5.676875
H	-3.825998	0.7888955	-6.0686785
H	-5.3141905	2.5028805	-7.0975435
H	-6.3453995	2.558475	-8.416982
H	-6.9074265	1.996987	-6.934066
H	-3.3953445	0.929922	-8.724661
H	-3.8704745	-0.4943935	-9.476614
H	-4.4505125	0.986862	-10.0263875
H	-7.7628285	-1.1380995	-6.8736445
H	-8.452477	0.2491805	-7.531567
H	-8.8669335	-1.260789	-8.139844
H	-5.7759805	-1.999414	-9.7678665
H	-6.181386	-2.480139	-8.2063215
H	-7.3276355	-2.550921	-9.4393015
H	-8.2656585	-0.522144	-10.367046
H	-7.809189	0.9889135	-9.794761
H	-6.7303195	0.0686705	-10.704214
H	-5.572933	0.671895	-4.4945335
H	-5.30844	-0.9663165	-4.2990155
H	-4.2931475	0.277962	-2.5442485
H	-3.4535675	1.2003445	-3.6560175
H	-2.3408095	-2.6595055	-2.7713965
H	-3.7913715	-2.4767615	-3.580541
H	-3.6493895	-1.912255	-2.012912
H	-1.5311955	0.886232	-2.840107
H	-2.135121	-1.0749185	-0.767614
H	-2.8923145	0.3915635	-0.9832625
H	-0.8749575	1.534371	-0.628433
H	-0.18119	3.0037385	2.042972
H	-0.581076	2.261118	3.495131
H	-1.3931775	3.656205	3.021597
H	-2.3074385	3.3153475	-0.056305
H	-3.472369	3.647818	1.099501
H	-3.7106795	2.391008	0.011399
H	-3.9571555	-0.460984	1.492742
H	-5.0552825	-0.230614	2.7469725
H	-4.945519	0.902513	1.5117715
H	-3.3480425	2.5065615	4.3248005
H	-4.7139595	1.530281	4.370891
H	-4.552486	2.685614	3.162802
H	-2.1905045	-0.7220735	3.1882895
H	-1.946143	0.4746075	4.3469845
H	-3.3389625	-0.462543	4.391708
H	-0.166554	-1.4483625	1.127851
H	-0.2700045	-2.098183	-0.40907
H	1.23801	-1.8521055	0.263237

H	3.085748	-2.0656365	1.730352
H	4.5474145	-1.8829445	0.949816
H	4.9698845	-2.1378105	3.229648
H	3.866087	-0.952934	3.6390505
H	7.507049	0.1380305	2.1757775
H	7.171414	-1.489808	2.4816065
H	6.527108	-0.72846	1.122432
H	7.0429335	-2.661504	4.6461755
H	5.755501	-2.4400055	5.704429
H	7.3326345	-2.47287	6.2850005
H	9.2090485	-0.2289295	5.740734
H	8.729372	1.049486	4.759984
H	8.94556	-0.481895	4.1037705
H	6.1110725	2.4757195	7.4526615
H	7.467138	2.2334345	6.4932255
H	5.9427515	2.3137805	5.784898
H	8.0921585	0.2815845	7.8626695
H	6.9674485	-0.938543	8.1471255
H	6.7452725	0.5844045	8.817094
H	4.5362905	0.733402	7.8650435
H	4.296164	0.5241045	6.210456
H	4.708171	-0.7900275	7.1788475
H	4.2393145	1.357188	2.9018865
H	5.6971995	1.7499495	2.147168

Preparation of enone S10:

In an N_2-filled glovebox, a 500 mL round-bottom flask with a stir bar was charged with spiroketal **15** (1.70 g, 2.12 mmol, 1.0 equiv), "Cr (V)" (6.85 g, 21.2 mmol, 10 equiv), MnO_2 (3.69 g, 42.4 mmol, 20 equiv) and $(CH_2Cl)_2$/15-crown-5 (49:1, 140 mL, 0.015 M). The flask was removed from the glovebox and the resulting mixture was heated to 80 °C and stirred for 48 h. After cooling to room temperaure, the reaction was passed through a short pad of SiO_2 using 50% hexane/EtOAc as the eluent and concentrated in vacuo. The crude product was purified by flash column chromatography (0 to 5 to 10 to 15 to 20% EtOAc/hexanes) to afford starting spiroketal **15** (357 mg, 0.45 mmol, 21% yield) as a colorless foam and enone **S10** (1.04 g, 1.27 mmol, 60% yield) as a colorless foam.

Preparation of "Cr (V)": A 100 mL round-bottom flask was charged with $Na_2Cr_2O_7$•H_2O (ca. 8 g), heated to 100 °C for 2 h under high vacuum to afford anhydrous $Na_2Cr_2O_7$ (ca. 7.5 g). A 1 L flask was charged with anhydrous $Na_2Cr_2O_7$ (6.29 g, 24.0 mmol), 2-hydroxy-2-methylbutyric acid (17.0 g, 144 mmol, 6.0 equiv) and acetone (32 mL, 0.75 M). The resulting mixture was stirred at room temperature for 6 h. The resulting brown solid was collected by filtration, washed with acetone (2 × 10 mL). The crude product was

recrystalized with acetone (20 mL), collected by filtration, washed with acetone (2 × 10 mL), dried under high vacuum to afford "Cr (V)" (7.45 g, 23.0 mmol, 96% yield) as a brown solid.[6]

TLC (15% EtOAc/hexanes): R_f = 0.55 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (d, *J* = 1.4 Hz, 1H), 5.80 (dd, *J* = 2.1, 1.5 Hz, 1H), 4.65 (dd, *J* = 2.1, 1.0 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.68 (d, *J* = 11.6 Hz, 1H), 3.66 – 3.56 (m, 1H), 3.42 (dd, *J* = 11.6, 2.7 Hz, 1H), 3.07 (s, 1H), 2.82 – 2.75 (m, 1H), 2.46 – 2.43 (m, 1H), 2.42 (s, 1H), 2.12 (td, *J* = 13.2, 4.5 Hz, 1H), 1.96 (q, *J* = 6.9 Hz, 1H), 1.88 (m, 1H), 1.86 – 1.76 (m, 3H), 1.70 – 1.63 (m, 1H), 1.63 – 1.55 (m, 6H), 1.37 (ddd, *J* = 13.0, 4.3, 2.4 Hz, 1H), 1.30 (m, 1H), 1.25 (s, 2H), 1.21 (m, 1H), 1.16 (s, 3H), 1.11 (s, 3H), 1.09 (s, 3H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.90 – 0.88 (m, 27H), 0.10 (d, *J* = 0.7 Hz, 6H), 0.08 (d, *J* = 0.9 Hz, 6H), 0.06 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 196.72, 167.34, 145.79, 126.82, 123.69, 107.37, 94.10, 90.89, 73.81, 71.06, 69.90, 69.43, 56.70, 49.43, 48.11, 43.39, 42.70, 37.96, 36.14, 33.87, 31.76, 29.85, 27.50, 26.53, 26.18, 26.00, 25.97, 18.34, 18.30, 18.03, 13.76, 7.98, -2.03, -2.17, -3.33, -4.13, -4.51, -4.55.
FTIR (NaCl, thin film, cm^{-1}): 3522, 2949, 2931, 2856, 1681, 1470, 1462, 1373, 1252, 1086 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{45}H_{81}O_7Si_3$: 817.5290 $[M+H]^+$; found: 817.5270.
$[\alpha]_D^{21}$: +17° (*c* = 0.100, $CHCl_3$).

Table S2. Other attempted allylic oxidations

entry	conds.	X = O R = H (**S10**)	X = OH, H R = H	X = O R = OH	**15**
1	$Mn(OAc)_3$ (10 mol %), TBHP (10 equiv) 3Å MS, EtOAc, 22 °C	11%	–	–	–
2	$Rh_2(cap)_4$ (1 mol %), TBHP (10 equiv) K_2CO_3 (0.5 equiv), DCM, 22 °C	17%	–	–	–
3	$Rh_2(cap)_4$ (1 mol %), TBHP (10 equiv) DCE, 22 °C	17%	8%	1%	11%
4	CuI (70 mol %), TBAB (10 mol %) TBHP (30 equiv), DCm, 45 °C	10%	3%	2%	15%
5	$Na_2Cr_2O_7$ (1.5 equiv), Cl_4NHPI (2.2 equiv) acetone/py (9:1), 22 °C	3%	–	–	80%
6	$Na_2Cr_2O_7$ (1.5 equiv), Cl_4NHPI (2.2 equiv) acetone/py (19:1), 22 °C	37%	–	–	50%
7	$Na_2Cr_2O_7$ (1.5 equiv), Cl_4NHPI (2.2 equiv) acetone, 22 °C	22%	2%	2%	23%
8	PCC (30 equiv), NaOAc (30 equiv) celite (100 wt % PCC), PhH, 85 °C	1%	2%	2%	–
9	PDC (1.5 equiv), NHPI (1.5 equiv) MeCN/DCM/py/H_2O (9:9:1:1), 23 °C	29%	–	15%	–
10	PDC (1.5 equiv), NHPI (5.0 equiv) acetone/py (19:1), 23 °C	43%	–	–	17%
11	NHPI (20 mol %), $Co(OAc)_2$ (10 mol %) $Mn(OAc)_2$ (10 mol %), O_2, acetone, 22 °C	3%	10%	10%	0%
12	$PhI(OAc)_2$ (3.0 equiv), TBHP (4.0 equiv) K_2CO_3 (0.5 equiv), *n*-$PrCO_2Bu$/hexane, 0 °C	10%	1%	1%	4%
13	$NaClO_2$ (1.5 equiv), NHPI (10 mol %) MeCN/THF/H_2O, 50 °C	–	–	–	78%
14	"Cr(V)" (2.0 equiv), NHPI (5.0 equiv) acetone/py (19:1), 23 °C	29%	–	15%	18%
15	"Cr(V)" (5.0 equiv), MnO_2 (50 equiv) $PhCF_3$/15-c-5 (49:1), 80 °C	37%	–	1%	35%
16	"Cr(V)" (10 equiv), MnO_2 (20 equiv) $PhCF_3$/15-c-5 (49:1), 80 °C	41%	–	2%	22%
17	"Cr(V)" (10 equiv), MnO_2 (20 equiv) EtOAc/15-c-5 (49:1), 80 °C	23%	–	1%	44%
18	"Cr(V)" (10 equiv), MnO_2 (20 equiv) dioxane/15-c-5 (49:1), 80 °C	13%	–	–	61%
19	"Cr(V)" (10 equiv), MnO_2 (20 equiv) DCE/15-c-5 (49:1), 80 °C	60%	–	2%	5%

Preparation of C7 alcohol 16:

In a N_2-filled glovebox, a 200 mL round-bottom flask with a stir bar was charged with enone **S10** (147 mg, 0.18 mmol, 1.0 equiv), 2-naphthalene thiol (577 mg, 3.60 mmol, 20.0 equiv) and THF (3.6 mL, 0.05 M). Also in the glovebox, a 24 mL syringe was used to withdraw a premade SmI_2 solution (0.05 M in THF (6.1 mL 0.1M SmI_2 in THF + 6.1 mL THF), 36.0 mL, 1.8 mmol, 10.0 equiv). The flask and syringe were sealed and removed from the glovebox. The reaction flask was placed under N_2, stirred, and brought to –10 °C by lowering into a NaCl/ice water bath (~1:3 by mass). The SmI_2 solution was then added dropwise over 1 h via syringe pump, maintaining an ice bath temperature of –10 °C. Upon completion of the addition, the ice bath was removed and the reaction was allowed to come to room temperature and stirred for an additional 30 min. The reaction was quenched by addition of sat. aq. Rochelle's salt (30 mL) and 1M aq. NaOH (30 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). Combined organics were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (10 to 15 to 20% EtOAc/hexanes) to afford C7′ alcohol **16** (126 mg, 0.15 mmol, 85% yield, single isomer C5′ and C7′) as a colorless foam.

Preparation of SmI_2 solution in THF: A 125 mL sep-funnel was charged with $(CH_2I)_2$ (ca. 4 g), Et_2O (50 mL) and sat. aq. $Na_2S_2O_3$ (10 mL). The layers were separated, and the organic layer was further washed with sat. aq. $Na_2S_2O_3$ (4 × 10 mL) and H_2O (5 × 10 mL). Combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting material was dried under high vacuum in the dark for 15 min to afford purified $(CH_2I)_2$ (ca. 3.2 g) as a colorless crystal. In a N_2-filled glovebox, a 200 mL flask was charged with freshly purified $(CH_2I)_2$ (2.81 g, 10.0 mmol, 1.0 equiv), Sm (300 mesh, 3.01 g, 20.0 mmol, 2.0 equiv) and THF (100 mL). The resulting deep-green mixture was stirred at room temperature in the dark for 12 h to afford deep-blue SmI_2 solution (0.1 M in THF), which is usable for several months.

TLC (15% EtOAc/hexanes): R_f = 0.26 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.54 (t, *J* = 1.5 Hz, 1H), 4.67 (d, *J* = 2.3 Hz, 1H), 4.00 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.74 (ddd, *J* = 10.9, 9.4, 5.1 Hz, 1H), 3.67 (d, *J* = 11.6 Hz, 1H), 3.54 (h, *J* = 5.3 Hz, 1H), 3.45 (dd, *J* = 11.6, 2.7 Hz, 1H), 3.16 (s, 1H), 2.20 – 2.11 (m, 1H), 1.99 (t, *J* = 9.4 Hz, 1H), 1.91 (q, *J* = 6.9 Hz, 1H), 1.83 – 1.57 (m, 7H), 1.54 – 1.44 (m, 2H), 1.44 – 1.37 (m, 3H), 1.35 – 1.32 (m, 1H), 1.32 – 1.29 (m, 1H), 1.27 – 1.24 (m, 1H), 1.17 (dt, *J* = 11.5, 2.5 Hz, 1H), 1.12 (s, 3H), 1.06 (s, 3H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.97 – 0.91 (m, 1H), 0.89 (s, 9H), 0.88 (s, 9H), 0.88 (s, 9H), 0.86 (s, 3H), 0.84 – 0.78 (m, 1H), 0.78 – 0.72 (m, 1H), 0.10 (s, 3H), 0.08 (d, *J* = 1.6 Hz, 6H), 0.07 (s, 3H), 0.05 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 152.81, 119.21, 107.31, 93.61, 91.29, 74.76, 71.87, 70.47, 69.90, 69.35, 56.66, 50.52, 48.36, 43.00, 42.01, 38.19, 36.85, 35.99, 35.60, 34.03, 31.85, 31.28, 27.74, 26.55, 26.16, 26.06, 25.99, 18.38, 18.33, 18.25, 14.50, 12.50, 8.01, -2.03, -2.19, -3.02, -4.19, -4.45.
FTIR (NaCl, thin film, cm^{-1}): 3522, 2953, 2926, 2853, 2243, 1471, 1462, 1372, 1251, 1091, 1061 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{45}H_{83}O_7Si_3$: 819.5447 $[M+H–H_2]^+$; found: 819.5470.
$[\alpha]_D^{21}$: +45° (*c* = 0.167, $CHCl_3$).

Table S3. Optimization of SmI_2 double reduction

entry	conds.	X = β-OH, H (**16**)	X = α-OH, H	X = O	**S11**	**S10**
1	Pt/C (250 wt %), H_2 (balloon) EtOH, 22 °C	36%	–	11%	–	–
2	Pt/C (250 wt %), H_2 (balloon) EtOAc, 22 °C	–	–	–	45%	–
3	Pt/C (250 wt %), H_2 (balloon) hexane, 22 °C	–	–	–	51%	–
4	Pd/C (250 wt %), H_2 (balloon) *i*-PrOH, 22 °C	–	–	–	38%	–
5	Pd/C (20 wt %), H_2 (balloon) EtOH, 22 °C	17%	9%	25%	–	–
6	Li(0) (100 equiv), $FeCl_2{\cdot}4H_2O$ (10 equiv) THF, 22 °C	–	–	–	–	–
7	SmI_2 (10 equiv), t-BuOH (20 equiv) THF, –78 to 22 °C	–	–	–	–	36%
8	SmI_2 (10 equiv), PhSH (20 equiv) THF, –78 to 22 °C	–	–	60%	–	–
9	SmI_2 (10 equiv), PhSH (20 equiv) THF, 22 °C	75%	–	5%	–	–
10	SmI_2 (10 equiv), PhSH (20 equiv) Et_3N (20 equiv), THF, 22 °C	44%	–	21%	–	–
11	SmI_2 (10 equiv), TripSH (20 equiv) THF, 22 °C	74%	–	21%	–	–
12	SmI_2 (10 equiv), PhSH (20 equiv) THF, 28 °C[a]	77%	–	–	11%	–
13	SmI_2 (10 equiv), 2-NaphthSH (20 equiv) THF, 28 °C[a]	78%	–	–	10%	–
14	SmI_2 (10 equiv), 2-NaphthSH (20 equiv) THF, 0 °C	83%	–	–	5%	–
15	SmI_2 (10 equiv), 2-NaphthSH (20 equiv) THF, –15 °C	85%	–	–	–	–

[a]Glove box temperature.

Characterization data for **S11**

TLC (15% EtOAc/hexanes): R_f = 0.22 (*p*-anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 – 3.92 (m, 2H), 3.82 (q, *J* = 2.7 Hz, 1H), 3.59 (dd, *J* = 11.4, 5.5 Hz, 2H), 3.38 – 3.32 (m, 1H), 2.16 – 2.11 (m, 1H), 2.10 – 2.06 (m, 1H), 2.02 (d, *J* = 7.2 Hz, 1H), 1.99 – 1.94

(m, 1H), 1.94 – 1.88 (m, 1H), 1.78 (dd, J = 13.3, 4.4 Hz, 1H), 1.75 – 1.71 (m, 2H), 1.71 – 1.67 (m, 1H), 1.65 – 1.60 (m, 2H), 1.60 – 1.58 (m, 2H), 1.56 – 1.53 (m, 1H), 1.53 – 1.50 (m, 1H), 1.48 (d, J = 2.4 Hz, 1H), 1.46 (t, J = 2.7 Hz, 1H), 1.44 – 1.41 (m, 2H), 1.41 – 1.37 (m, 2H), 1.37 – 1.31 (m, 3H), 1.30 – 1.26 (m, 2H), 1.25 (s, 2H), 1.24 – 1.20 (m, 2H), 1.12 (d, J = 1.2 Hz, 1H), 1.11 (s, 1H) 1.07 – 0.98 (m, 2H), 0.98 – 0.94 (m, 1H), 0.94 (d, J = 7.2 Hz, 3H), 0.90 (m, 2H), 0.89 (s, 9H), 0.88 (s, 9H), 0.88 (s, 9H), 0.87 (d, J = 2.5 Hz, 2H), 0.81 (s, 3H), 0.77 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 110.15, 90.42, 90.39, 72.04, 72.00, 69.39, 69.36, 67.74, 50.24, 45.99, 45.18, 44.58, 38.62, 38.19, 37.34, 36.94, 36.57, 35.67, 33.85, 31.98, 30.64, 30.50, 27.13, 26.52, 26.39, 26.10, 26.07, 25.98, 18.41, 18.33, 11.40, 11.37, 8.09, -2.02, -2.17, -2.98, -3.38, -4.43.

FTIR (NaCl, thin film, cm^{-1}): 3470, 2952, 2929, 2856, 1472, 1462, 1372, 1252, 1076, 1055 cm^{-1}.

HRMS (FAB+, m/z): calc'd for $C_{45}H_{85}O_7Si_3$: 821.5603 $[M+H–H_2]^+$; found: 821.5611.

$[\alpha]_D^{21}$: –103° (c = 0.208, $CHCl_3$).

Minimized Structures and energies (see also Figure S1):

S11a

Single-point energy = -3160.596228982013 (Hartree)
N_atoms = 141
C 3.6828335 -1.566169 -0.698298
C 3.2484025 -0.2333645 -1.080993
C 2.0359535 0.277253 -0.393421
O 1.9947235 -0.132346 0.908973
C 2.238595 1.7602055 -0.439994
C 1.1002695 2.34322 -1.1341905
C 0.0457595 1.388837 -0.7640805
C -1.3193675 1.517233 -1.2832235
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O -1.2040675 3.826385 -1.78369
C -3.305516 2.920781 -1.4064395
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C -3.803509 0.1571735 -2.3811575
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C -0.147479 -0.9577595 -0.3338695
O 0.336949 -2.205157 -0.61305
Si 0.049404 -3.652758 0.01298

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C	-0.850646	-2.952039	2.507906
C	0.092221	-5.129185	2.2618995
C	1.51949	-3.2074715	2.263612
C	0.6795835	0.0570365	-1.006641
C	0.781053	-0.24966	-2.4386995
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C	4.196928	0.863041	-0.8500925
C	5.3609245	0.9375775	-1.714233
C	6.266658	2.008159	-1.3029195
C	6.628472	1.9001905	0.116312
C	7.375933	3.077253	0.5483615
O	7.3649115	0.755355	0.2395915
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C	7.8614825	0.392704	3.0070025
C	10.018068	0.953831	1.1133865
C	8.4986015	-1.6042745	0.8797605
C	9.5210035	-2.2728475	1.6985345
C	8.844512	-1.7611275	-0.5401485
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O	4.596287	0.752226	0.469909
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H	3.911267	-1.6223715	0.3115955
H	4.528986	-1.8465035	-1.2363785
H	3.0836515	-0.221722	-2.1068175
H	2.826817	0.0969995	1.2506865
H	2.2654125	2.1066575	0.544933
H	1.2713075	2.3584915	-2.1606155
H	0.891314	3.314646	-0.8406255
H	-0.046879	1.4691115	0.2771535
H	-1.318746	1.3359065	-2.31331
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H	-11.207162	0.954411	-1.9674045
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H	-10.311789	2.376156	-1.9177685

H	-11.4854725	1.948658	1.4720535
H	-11.462123	3.006599	0.162309
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H	1.6050965	-3.248823	3.3049755
H	2.299844	-3.776776	1.8720845
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H	1.197245	-1.1907855	-2.572741
H	1.362461	0.4414205	-2.952041
H	-0.1507885	-0.2599995	-2.897451
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H	5.0448685	1.085375	-2.695004
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H 7.2209575 -3.2433735 0.8329915
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H 5.5976565 1.5805665 1.890745
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S11b

Single-point energy = -3160.584909522271 (Hartree)
N_atoms = 141
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S11b

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C	6.2960885	-1.305408	2.492896
O	7.588235	-0.832692	0.5817995
Si	9.1096655	-1.181226	0.926164
C	9.2818705	-2.571221	2.060259
C	9.769062	-1.6736155	-0.6693495
C	10.014791	0.278687	1.5740765
C	11.4483945	-0.044003	1.6661995
C	9.537444	0.6525985	2.912475
C	9.8466285	1.4223805	0.6663865
C	5.43655	-1.3521725	0.2452345
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H	0.733201	-3.244081	-5.3713125
H	0.934591	-1.5757865	-5.3355655
H	1.7625055	-2.5366935	-4.2358505
H	-2.172201	-2.634027	-5.246616
H	-2.858181	-1.8799175	-3.912054
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H	1.2867455	-4.3818175	-2.6319785
H	0.4097775	-5.0146495	-1.347471
H	0.9090615	-3.3994955	-1.3260835
H	-1.501059	-2.9433395	-0.832852
H	-2.673496	-3.332499	-1.9756275
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H	-1.216834	-5.765597	-2.9633355
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H	0.0235205	1.9210535	-2.5420825
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H	4.359519	1.9494925	1.387184
H	6.6143735	1.2413395	1.8648275
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H	5.315227	-1.3035385	2.8359785
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H	6.610466	-2.295298	2.453031
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H	8.748434	-3.3966105	1.715495
H	9.6551945	-0.9239755	-1.381818
H	10.781023	-1.9129465	-0.61507
H	9.2643415	-2.5148105	-1.0185305
H	11.8587835	-0.2759705	0.737468
H	11.632326	-0.8465515	2.304843
H	11.9789865	0.774797	2.0400865
H	8.5288705	0.9125505	2.9109565
H	9.668334	-0.116766	3.602687
H	10.065938	1.4802975	3.269849
H	10.2122255	1.217102	-0.287348
H	8.8477235	1.696837	0.5673995
H	10.368508	2.253559	1.0255505
H	5.638024	-1.000488	-0.7150055

H 5.585593 -2.382277 0.2528335

Preparation of C3 alcohol 17:

A 25 mL round-bottom flask with a stir bar was charged with charged with C7′ alcohol **16** (50 mg, 0.06 mmol), 2,6-lutidine (19.8 µL, 0.17 mmol, 3.0 equiv) and CH_2Cl_2 (5.8 mL, 0.01 M). TIPSOTf (23.4 µL, 0.087 mmol, 1.5 equiv) was added dropwise at room temperature. After stirring for 30 min, Et_3N•3HF (186 µL, 1.16 mmol, 20 equiv) was added dropwise and stirred at room temparature for 12 h. The reaction was diluted with hexane (6 mL), quenched with H_2O (6 mL). The layers were separated. The aqueous layer was further extracted with hexane (3 × 6 mL), combined organic layers were washed with st. $NaHCO_3$ aq. (6 mL) and brine (6 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (10 to 15 to 20 % EtOAc/hexanes) to afford C3′ alcohol **17** (50.5 mg, 0.058 mmol, 96% yield) as a colorless foam.

TLC (20% EtOAc/hexanes): R_f = 0.31 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.47 (t, *J* = 1.7 Hz, 1H), 4.74 (d, *J* = 1.9 Hz, 1H), 3.91 (ddd, *J* = 22.1, 10.5, 5.1 Hz, 2H), 3.70 (d, *J* = 11.7 Hz, 1H), 3.58 (tt, *J* = 10.6, 4.6 Hz, 1H), 3.44 (dd, *J* = 11.7, 2.7 Hz, 1H), 3.34 (s, 1H), 2.15 – 2.05 (m, 1H), 1.96 (t, *J* = 10.5 Hz, 1H), 1.89 – 1.84 (m, 1H), 1.83 – 1.79 (m, 1H), 1.79 – 1.70 (m, 2H), 1.66 – 1.63 (m, 1H), 1.63 – 1.53 (m, 5H), 1.46 – 1.40 (m, 2H), 1.40 – 1.34 (m, 2H), 1.34 – 1.29 (m, 1H), 1.25 (s, 3H), 1.22 (dd, *J* = 4.1, 2.4 Hz, 1H), 1.21 – 1.13 (m, 2H), 1.11 (s, 3H), 1.05 (s, 4H), 1.03 (s, 3H), 1.03 – 1.03 (m, 6H), 1.02 (s, 6H), 1.01 (d, *J* = 1.5 Hz, 2H), 0.94 (dd, *J* = 13.5, 4.0 Hz, 1H), 0.89 (s, 9H), 0.88 (s, 9H), 0.86 (s, 3H), 0.82 – 0.77 (m, 1H), 0.77 – 0.71 (m, 1H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.07 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.67, 120.54, 107.03, 93.71, 91.87, 75.58, 71.31, 71.15, 69.91, 69.44, 56.48, 51.33, 48.41, 43.39, 41.89, 38.30, 38.00, 36.75, 35.36, 33.96, 31.66, 31.39, 29.85, 28.20, 26.58, 26.20, 26.01, 18.71, 18.69, 18.34, 18.28, 13.48, 13.25, 12.63, 8.10, -2.02, -2.19, -2.84, -4.25.
FTIR (NaCl, thin film, cm^{-1}): 3521, 2927, 2862, 1470, 1462, 1384, 1252, 1117, 1088, 1058 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{48}H_{90}O_7Si_3$: 862.5994 [M+•]$^-$; found: 862.6001.
$[\alpha]_D^{21}$: +33° (*c* = 0.125, $CHCl_3$).

Preparation of ketone 2:

A 10 mL round-bottom flask with a stir bar was charged with C3′ alcohol **17** (29.0 mg, 0.035 mmol, 1.0 equiv), $Cu(MeCN)_4OTf$ (1.3 mg, 3.50 μmol, 10 mol %), ^{MeO}bpy (0.76 mg, 3.50 μmol, 10 mol %), ABNO (0.50 mg, 3.50 μmol, 10 mol %), NMI (0.56 μL, 7.00 μmol, 20 mol %) and MeCN/THF (3:1, 3.5 mL, 0.01 M). The resulting solution was sparged with O_2 for 5 min, then vigurously stirred (1200 rpm) at room temperature under O_2 atmosphere for 12 h. The reaction was passed through a short pad of SiO_2 using 50% EtOAc/hexanes as the eluent and concentrated in vacuo. The crude product was purified by flash column chromatography (10 to 15 to 20% EtOAc/hexanes) to afford western fragment **2** (28.9 mg, 0.034 mmol, 99% yield) as a colorless foam.

TLC (15% EtOAc/hexanes): R_f = 0.53 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 (t, *J* = 1.7 Hz, 1H), 4.73 (d, *J* = 2.0 Hz, 1H), 3.99 – 3.86 (m, 2H), 3.70 (d, *J* = 11.7 Hz, 1H), 3.43 (dd, *J* = 11.7, 2.7 Hz, 1H), 3.24 (s, 1H), 2.43 – 2.32 (m, 2H), 2.32 – 2.26 (m, 1H), 2.16 – 2.06 (m, 2H), 2.02 (t, *J* = 10.5 Hz, 1H), 1.91 (ddd, *J* = 14.6, 6.8, 3.1 Hz, 1H), 1.86 (q, *J* = 6.9 Hz, 1H), 1.82 – 1.76 (m, 1H), 1.76 – 1.72 (m, 1H), 1.67 (ddd, *J* = 12.3, 4.9, 2.3 Hz, 1H), 1.62 – 1.59 (m, 1H), 1.58 – 1.53 (m, 2H), 1.50 – 1.41 (m, 2H), 1.33 – 1.24 (m, 3H), 1.23 – 1.18 (m, 1H), 1.11 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H), 1.05 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 1.3 Hz, 3H), 1.03 – 1.02 (m, 12H), 1.01 (d, *J* = 1.3 Hz, 3H), 0.89 (s, 9H), 0.88 (s, 9H), 0.87 – 0.84 (m, 1H), 0.10 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 210.91, 150.19, 120.90, 107.10, 93.69, 91.79, 75.06, 70.86, 69.90, 69.43, 56.43, 50.57, 48.33, 44.33, 43.71, 43.22, 38.35, 38.06, 37.99, 35.49, 33.91, 32.01, 29.86, 28.03, 26.57, 26.21, 26.01, 18.69, 18.67, 18.34, 18.29, 13.49, 13.22, 11.79, 8.08, -2.02, -2.19, -3.00, -4.24.
FTIR (NaCl, thin film, cm^{-1}): 3524, 2932, 2860, 1715, 1470, 1462, 1384, 1252, 1113, 1089, 1056 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{48}H_{87}O_7Si_3$: 859.5760 $[M+H–H_2]^+$; found: 859.5757.
$[\alpha]_D^{21}$: +70° (*c* = 0.167, $CHCl_3$).

Preparation of α-bromo ketone S12:

A 25 mL round-bottom flask with a stir bar was charged with ketone **2** (27.0 mg, 0.031 mmol, 1.0 equiv) and THF (1.5 mL, 0.01 M total). The resulting solution was cooled to 0 °C and stirred at this temperature for 5 min. $PhNMe_3Br_3$ (12.2 mg, 0.33 mmol, 1.05 equiv) in THF (1.5 mL, 0.01 M total) was also cooled to 0 °C and was added by cannula in one portion, and the reaction was stirred at 0 °C for 30 min. The reaction was quenched with st. $Na_2S_2O_3$ aq. (1.5 mL) and H_2O (1.5 mL), diluted with hexane (3 mL). The layers were separated. The aqueous layer was further extracted with hexane (3 × 3 mL), combined organic layers were washed with brine (3 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (5 to 10 to 15% EtOAc/hexanes) to afford α-bromo ketone **S12** (24.4 mg, 0.026 mmol, 84% yield) as a colorless foam.[7]

TLC (10% EtOAc/hexanes): R_f = 0.35 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.47 (t, *J* = 1.7 Hz, 1H), 4.77 – 4.65 (m, 2H), 3.92 (ddd, *J* = 18.4, 10.4, 5.1 Hz, 2H), 3.69 (d, *J* = 11.6 Hz, 1H), 3.43 (dd, *J* = 11.7, 2.7 Hz, 1H), 3.15 (s, 1H), 2.52 – 2.43 (m, 2H), 2.16 – 2.06 (m, 1H), 1.99 (t, *J* = 10.6 Hz, 1H), 1.85 (q, *J* = 6.9 Hz, 1H), 1.82 – 1.73 (m, 2H), 1.73 – 1.64 (m,

3H), 1.64 – 1.54 (m, 3H), 1.52 – 1.42 (m, 2H), 1.26 (s, 2H), 1.24 – 1.14 (m, 2H), 1.14 (s, 3H), 1.11 (s, 3H), 1.08 (d, J = 4.9 Hz, 1H), 1.07 (s, 3H), 1.05 (d, J = 6.9 Hz, 4H), 1.02 (s, 9H), 1.01 (s, 6H), 1.00 (s, 3H), 0.91 (d, J = 3.0 Hz, 1H), 0.90 (s, 6H), 0.89 (s, 1H), 0.88 (s, 9H), 0.10 (s, 6H), 0.08 (d, J = 1.5 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.38, 149.77, 121.05, 107.16, 93.68, 91.72, 74.54, 70.57, 69.90, 69.42, 56.38, 53.75, 50.81, 50.20, 48.24, 44.33, 43.52, 42.79, 38.66, 37.81, 33.87, 32.12, 29.85, 27.85, 26.55, 26.21, 26.01, 18.67, 18.65, 18.34, 18.30, 13.55, 13.18, 12.43, 8.07, -2.01, -2.18, -3.04, -4.24.
FTIR (NaCl, thin film, cm^{-1}): 3519, 2924, 2862, 1728, 1470, 1462, 1387, 1254, 1089, 1062 cm^{-1}.
HRMS (TOF-ESI, m/z): calc'd for $C_{48}H_{88}O_7BrSi_3$: 939.5021 $[M+H]^+$; found: 939.5021.
$[\alpha]_D^{21}$: +39° (c = 0.250, $CHCl_3$).

Preparation of western fragment α-azido ketone 18:

In an N_2-filled glovebox, a 10 mL round-bottom flask with a stir bar was charged with α-bromo ketone **S12** (21 mg, 0.023 mmol) and n-$PrNO_2$ (2.3 mL, 0.01). $TMGN_3$ (14.3 mg, 0.09 mmol, 4.0 equiv) was added, and the reaction was stirred at room temperature for 4 h. Upon completion, the reaction was diluted with heptane (2.3 mL) and was concentrated in vacuo. The crude material was azeotroped with another 2.3 mL of heptane to remove n-$PrNO_2$. The crude product was purified by flash column chromatography (5 to 10 to 15% EtOAc/hexanes) to afford α-azido ketone **18** (15.8 mg, 0.017 mmol, 76% yield) as a colorless foam.[7]

TLC (10% EtOAc/hexanes): R_f = 0.40 (p-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.47 (t, J = 1.6 Hz, 1H), 4.71 (d, J = 2.0 Hz, 1H), 4.04 – 3.85 (m, 3H), 3.69 (d, J = 11.6 Hz, 1H), 3.43 (dd, J = 11.7, 2.7 Hz, 1H), 3.15 (s, 1H), 2.42 (t, J = 14.1 Hz, 1H), 2.29 (dd, J = 14.5, 3.8 Hz, 1H), 2.17 (dd, J = 12.7, 6.2 Hz, 1H), 2.12 – 2.06 (m, 1H), 2.00 (t, J = 10.5 Hz, 1H), 1.85 (q, J = 6.9 Hz, 1H), 1.79 (dd, J = 13.3, 4.2 Hz, 1H), 1.73 (t, J = 4.6 Hz, 1H), 1.70 (t, J = 5.0 Hz, 1H), 1.61 (m, 3H), 1.52 –1.38 (m, 3H), 1.29 (d, J = 12.9 Hz, 2H), 1.25 (s, 3H), 1.20 (ddd, J = 12.8, 4.2, 2.4 Hz, 2H), 1.13 (s, 3H), 1.11 (s, 3H), 1.07 (s, 3H), 1.05 (d, J = 6.9 Hz, 5H), 1.03 (t, J = 1.4 Hz, 9H), 1.02 (s, 6H), 1.00 (d, J = 1.4 Hz, 3H), 0.89 (s, 9H), 0.88 (s, 9H), 0.87 – 0.85 (m, 1H), 0.10 (d, J = 1.2 Hz, 6H), 0.07 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.52, 149.82, 121.03, 107.16, 93.68, 91.72, 74.55, 70.61, 69.90, 69.42, 63.63, 56.38, 50.29, 48.24, 44.69, 44.39, 43.40, 42.74, 37.80, 36.67, 33.87, 32.18, 29.86, 27.86, 26.55, 26.21, 26.01, 18.67, 18.66, 18.35, 18.30, 13.54, 13.18, 12.79, 8.07, 1.17, -2.01, -2.18, -3.07, -4.25.
FTIR (NaCl, thin film, cm^{-1}): 3526, 2928, 2857, 2106, 1732, 1463, 1386, 1252, 1090, 1056 cm^{-1}.
HRMS (TOF-ESI, m/z): calc'd for $C_{48}H_{88}N_3O_7Si_3$: 902.5930 $[M+H]^+$; found: 902.5936.
$[\alpha]_D^{21}$: +45° (c = 0.083, $CHCl_3$).

2v. Synthesis of eastern amino methoxime 21

Preparation of homopropargyl alcohol 14:

A 1 L round-bottom flask with a stir bar was charged with α-hydroxy ketone **12** (6.78 g, 12.4 mmol, 1.0 equiv), propargyl bromide **7** (5.13 g, 18.6 mmol, 1.5 equiv) and CH_2Cl_2 (250 mL, 0.05 M). The resulting solution was cooled to –78 °C and stirred at this temperature for 30 min. Thereafter, *n*-BuLi (2.5 M in hexane, 5.21 mL, 13.02 mmol, 1.05 equiv) was added dropwise at –78 °C. After stirring at –78 °C for 15 min, Ti(O*i*-Pr)$_4$ (7.34 mL, 24.8 mmol, 2.0 equiv) was added dropwise at –78 °C. After stirring at –78 °C for 15 min, *i*-PrMgCl (2.0 M in Et_2O, 24.8 mL, 49.6 mmol, 4.0 equiv) was added dropwise at –78 °C. The reaction was stirred at –78 °C for 30 min, then warmed to room temperature. After stirring at room temperature for 12 h, the reaction was diluted with Et_2O (150 mL), quenched with st. NH_4Cl aq. (150 mL) and H_2O (150 mL). After vigorously stirring for 3 h, the resulting solid was
removed by filtration, washed with Et_2O (2 × 50 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 150 mL), combined organic layers were washed with brine (2 × 150 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (5 to 10 to 15% EtOAc/hexanes) to afford homopropargyl alcohol **14** (5.17 g, 6.94 mmol, 1:1 mixture of diastereomers at C20, 56% yield) as a colorless foam.

TLC (10% EtOAc/hexanes): R_f = 0.48 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 – 5.32 (m, 2H), 5.26 (t, *J* = 1.9 Hz, 1H), 5.18 (t, *J* = 1.8 Hz, 1H), 4.79 (d, *J* = 13.2 Hz, 2H), 4.31 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.20 (dd, *J* = 11.5, 4.2 Hz, 1H), 3.68 (s, 1H), 3.54 – 3.41 (m, 3H), 3.38 (s, 1H), 3.31 (d, *J* = 4.6 Hz, 1H), 3.21 (qt, *J* = 7.1, 2.4 Hz, 1H), 2.84 (qt, *J* = 7.0, 2.4 Hz, 1H), 2.64 (s, 1H), 2.31 (dd, *J* = 8.5, 2.3 Hz, 5H), 2.25 (d, *J* = 2.5 Hz, 1H), 2.23 (d, *J* = 2.4 Hz, 1H), 2.20 (d, *J* = 5.4 Hz, 2H), 2.18 – 2.13 (m, 2H), 2.13 – 2.07 (m, 2H), 2.05 – 2.02 (m, 1H), 2.02 – 1.98 (m, 1H), 1.98 – 1.93 (m, 1H), 1.81 – 1.78 (m, 1H), 1.76 (s, 3H), 1.74 – 1.69 (m, 3H), 1.67 (t, *J* = 4.3 Hz, 1H), 1.61 – 1.54 (m, 4H), 1.51 (dt, *J* = 7.5, 3.1 Hz, 3H), 1.47 (d, *J* = 8.6 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.33 (s, 3H), 1.31 (dd, *J* = 2.9, 1.8 Hz, 12H), 1.25 (s, 3H), 1.12 (d, *J* = 3.0 Hz, 4H), 1.08 (s, 4H), 1.06 – 1.04 (m, 2H), 1.02 (s, 3H), 1.01 (s, 3H), 0.93 – 0.92 (m, 2H), 0.91 (s, 9H), 0.90 (s, 9H), 0.89 (s, 18H), 0.15 (s, 9H), 0.12 (d, *J* = 1.2 Hz, 12H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 – 0.05 (m, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.03, 153.53, 140.69, 123.00, 121.95, 120.85, 120.82, 86.16, 83.93, 82.55, 82.24, 81.79, 79.72, 78.86, 76.51, 73.89, 73.86, 72.75, 72.57, 71.83, 58.17, 56.88, 47.67, 47.30, 42.73, 37.08, 37.05, 36.96, 35.55, 35.53, 33.54, 33.17, 32.09, 31.06, 30.25, 30.07, 29.86, 29.69, 29.62, 29.55, 29.51, 29.37, 29.05, 26.37, 26.19, 26.08, 19.32, 19.26, 18.46, 18.41, 18.24, 17.42, 15.08, 14.87, 2.66, -3.07, -3.38, -3.74, -3.80, -4.43.
FTIR (NaCl, thin film, cm^{-1}): 3472, 2927, 2854, 1748, 1722, 1470, 1463, 1371, 1248, 1049 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{42}H_{75}O_5Si_3$: 743.4922 $[M+H–H_2]^+$; found: 743.4940.
$[\alpha]_D^{21}$: –123° (*c* = 0.222, $CHCl_3$).

Preparation of triol S13:

A 500 mL round-bottom flask with a stir bar was charged with α-hydroxy enone **14** (4.13 g, 5.55 mmol, 1:1 mixture of diastereomers at C20) and MeOH (185 mL, 0.03 M). K_2CO_3 (3.84 g, 27.8 mmol, 5.0 equiv) was added in one portion and stirred at room temperature for 12 h. The reaction was quenched with st. NH_4Cl aq. (50 mL) and H2O (50 mL). The resulting mixture was concentrated in vacuo to remove most of the MeOH. EtOAc (100 mL) was added, the layers were separated. The aqueous layer was further extracted with EtOAc (3 × 100 mL), combined organic layers were washed with brine (2 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (20 to 30 to 40% EtOAc/hexanes) to afford tertiary alcohol **S13** (3.64 g, 4.88 mmol, 1:1 mixture of diastereomers at C20, 88% yield) as a colorless foam.

TLC (20% EtOAc/hexanes): R_f = 0.19 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.38 – 5.33 (m, 2H), 5.31 (t, *J* = 1.9 Hz, 1H), 5.23 (t, *J* = 1.9 Hz, 1H), 4.82 – 4.70 (m, 2H), 4.28 (dd, *J* = 11.4, 4.6 Hz, 1H), 4.16 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.92 (s, 1H), 3.53 –3.43 (m, 3H), 3.23 – 3.12 (m, 1H), 2.85 (qt, *J* = 7.0, 2.4 Hz, 1H), 2.74 (s, 1H), 2.33 (dd, *J* = 6.6, 2.4 Hz, 4H), 2.30 – 2.27 (m, 1H), 2.27 – 2.24 (m, 1H), 2.24 – 2.18 (m, 3H), 2.18 – 2.13 (m, 1H), 2.13 – 2.07 (m, 2H), 2.06 – 2.03 (m, 1H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.78 (q, *J* = 3.5 Hz, 1H), 1.76 – 1.74 (m, 2H), 1.72 (d, *J* = 4.1 Hz, 2H), 1.69 (t, *J* = 4.3 Hz, 1H), 1.61 – 1.55 (m, 5H), 1.55 – 1.46 (m, 3H), 1.34 (d, *J* = 2.9 Hz, 3H), 1.33 (d, *J* = 2.9 Hz, 3H), 1.30 – 1.28 (m, 9H), 1.28 (s, 4H), 1.25 (s, 2H), 1.13 (s, 3H), 1.11 (s, 1H), 1.10 (s, 3H), 1.09 – 1.05 (m, 2H), 1.05 – 1.04 (m, 1H), 1.02 (s, 3H), 1.01 (s, 3H), 0.91 (s, 9H), 0.90 (s, 9H), 0.89 (s, 18H), 0.12 (s, 3H), 0.11 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.06 (s, 12H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.39, 154.16, 140.67, 140.64, 122.89, 122.18, 120.82, 120.76, 86.75, 85.79, 82.71, 82.48, 80.21, 79.43, 78.05, 76.43, 73.57, 72.54, 72.52, 72.45, 70.35, 70.09, 58.06, 56.66, 47.89, 47.48, 42.70, 37.12, 37.09, 37.00, 34.62, 34.34, 33.82, 33.25, 32.07, 32.05, 30.96, 30.23, 30.17, 30.13, 29.24, 29.10, 28.98, 28.88, 28.82, 28.78, 26.33, 26.12, 26.08, 19.32, 19.31, 19.01, 18.44, 18.40, 18.21, 17.38, 14.88, 14.49, -3.14, -3.28, -3.65, -3.92, -4.44.
FTIR (NaCl, thin film, cm^{-1}): 3382, 2932, 2854, 1704, 1470, 1462, 1379, 1252, 1098, 1084 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{39}H_{67}O_5Si_2$: 671.4527 $[M+H–H_2]^+$; found: 671.4547.
$[\alpha]_D^{21}$: –91° (*c* = 0.200, $CHCl_3$).

Preparation of α-hydroxy enone 19:

A 500 mL round-bottom flask with a stir bar was charged with homopropargyl alcohol **S13** (3.15 g, 4.69 mmol, 1:1 mixture of diastereomers at C20), $Cu(MeCN)_4OTf$ (177 mg, 0.47 mmol, 10 mol %), ^{MeO}bpy (102

mg, 0.47 mmol, 10 mol %), ABNO (65.9 mg, 0.47 mmol, 10 mol %), NMI (74.9 µL, 0.94 mmol, 20 mol %) and MeCN/THF (3:1, 160 mL, 0.03 M). The resulting solution was sparged with O_2 for 5 min, then vigurously stirred (1200 rpm) at room temperature under O_2 atmosphere for 12 h. The reaction was passed through a short pad of SiO_2 using 50% EtOAc/hexanes as the eluent and concentrated in vacuo. The crude product was purified by flash column chromatography (15 to 25 to 35% EtOAc/hexanes) to afford α-hydroxy enone **19** (2.89 g, 4.31 mmol, 1:1 mixture of diastereomers at C20, 92% yield) as a colorless foam.

TLC (30% EtOAc/hexanes): R_f = 0.47 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (dd, *J* = 10.6, 1.5 Hz, 2H), 5.42 – 5.37 (m, 2H), 3.95 (ddd, *J* = 11.1, 5.1, 4.0 Hz, 2H), 3.58 (s, 1H), 3.55 – 3.41 (m, 4H), 3.01 (qt, *J* = 7.1, 2.4 Hz, 1H), 2.83 – 2.75 (m, 1H), 2.53 (qd, *J* = 11.3, 4.9 Hz, 2H), 2.39 – 2.31 (m, 2H), 2.29 (d, *J* = 2.4 Hz, 3H), 2.25 (q, *J* = 2.4 Hz, 5H), 2.21 (dd, *J* = 5.6, 1.9 Hz, 1H), 2.18 – 2.05 (m, 4H), 1.85 – 1.80 (m, 2H), 1.78 (d, *J* = 5.1 Hz, 3H), 1.76 – 1.71 (m, 5H), 1.71 – 1.68 (m, 2H), 1.67 – 1.63 (m, 3H), 1.61 (d, *J* = 3.6 Hz, 3H), 1.59 – 1.56 (m, 3H), 1.56 – 1.50 (m, 3H), 1.47 (s, 6H), 1.42 (d, *J* = 7.0 Hz, 4H), 1.32 – 1.29 (m, 6H), 1.28 – 1.27 (m, 3H), 1.25 (s, 9H), 1.24 (s, 6H), 1.21 (s, 4H), 1.20 (s, 4H), 1.18 – 1.16 (m, 2H), 1.15 – 1.12 (m, 2H), 1.11 (d, *J* = 1.5 Hz, 6H), 1.10 – 1.08 (m, 2H), 1.08 – 1.04 (m, 3H), 1.01 (d, *J* = 1.6 Hz, 1H), 0.91 (d, *J* = 1.4 Hz, 3H), 0.91 (s, 6H), 0.90 (s, 3H), 0.89 (s, 24H), 0.88 (d, *J* = 1.2 Hz, 3H), 0.10 (d, *J* = 1.7 Hz, 9H), 0.08 (s, 3H), 0.06 (d, *J* = 2.3 Hz, 15H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 206.85, 206.60, 187.25, 185.98, 140.79, 140.70, 125.25, 124.89, 119.90, 119.84, 85.54, 84.22, 82.25, 81.02, 80.90, 77.35, 77.03, 76.71, 76.20, 75.50, 72.16, 72.14, 70.02, 69.91, 55.74, 55.10, 48.26, 48.06, 42.50, 37.66, 37.07, 34.58, 33.31, 32.38, 32.24, 32.08, 31.89, 30.17, 30.02, 29.72, 28.61, 28.58, 28.55, 28.35, 28.12, 25.94, 25.92, 25.90, 19.34, 18.26, 18.13, 18.08, 15.84, 13.09, 12.19, -3.06, -3.37, -4.29, -4.53, -4.57, -4.60.
FTIR (NaCl, thin film, cm^{-1}): 3452, 2956, 2930, 2857, 1698, 1608, 1472, 1463, 1372, 1253, 1093 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{39}H_{67}O_5Si_2$: 671.4527 $[M+H]^+$; found: 671.4513.
$[\alpha]_D^{21}$: +24° (*c* = 0.222, $CHCl_3$).

Preparation of enone S14:

In a nitrogen-filled glovebox, a 500 mL round-bottom flask with a stir bar was charged with tertiary alcohol **19** (1.90 g, 2.84 mmol, 1:1 mixture of diastereomers at C20), HMPA (4.94 mL, 28.4 mmol, 10 equiv), H_2O (0.1 M in THF, 28.4 mL, 2.84 mmol, 1.0 equiv) and THF (115 mL, 0.025 M). SmI_2 solution (0.1 M in THF, 56.8 mL, 5.68 mmol, 2.0 equiv, see preparation procedure in preparation of **16**) was added dropwise over 20 min at room temperature. After stirring an additional 30 min, the reaction was diluted with EtOAc (50 mL), quenched with st. $NaHCO_3$ aq. (50 mL), st. $Na_2S_2O_3$ aq. (50 mL), H_2O (50 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 50 mL), combined organic layers were washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (15 to 20 to 25% EtOAc/hexanes) to afford enone **S14** (1.45 g, 2.22 mmol, 1:1 mixture of diastereomers at C20, 78% yield) as a colorless foam.

TLC (25% EtOAc/hexanes): R_f = 0.49 (*p*-anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (d, *J* = 1.7 Hz, 1H), 5.81 (d, *J* = 1.8 Hz, 1H), 5.41 – 5.35 (m, 2H), 3.48 (tt, *J* = 10.7, 5.0 Hz, 3H), 3.36 – 3.29 (m, 1H), 3.29 – 3.24 (m, 1H), 3.12 – 3.05 (m, 1H), 2.83 – 2.77 (m, 1H), 2.77 – 2.63 (m, 1H), 2.54 – 2.46 (m, 2H), 2.43 (d, *J* = 2.9 Hz, 1H), 2.32 – 2.29 (m, 1H), 2.28 (s, 3H), 2.26 – 2.25 (m, 1H), 2.25 – 2.20 (m, 6H), 2.20 – 2.14 (m, 2H), 2.12 (d, *J* = 1.9 Hz, 1H), 2.09 – 2.03 (m, 1H), 2.03 – 1.98 (m, 1H), 1.80 (q, *J* = 3.4 Hz, 1H), 1.78 (q, *J* = 2.7, 1.6 Hz, 2H), 1.75 (s, 2H), 1.72 – 1.65 (m, 5H), 1.61 (dd, *J* = 13.3, 4.5 Hz, 1H), 1.57 (s, 1H), 1.54 (d, *J* = 7.2 Hz, 4H), 1.53 – 1.49 (m, 1H), 1.45 – 1.38 (m, 1H), 1.34 (s, 3H), 1.32 (t, *J* = 4.0 Hz, 1H), 1.30 (d, *J* = 1.7 Hz, 3H), 1.29 – 1.27 (m, 1H), 1.26 (s, 3H), 1.25 (d, *J* = 4.3 Hz, 5H), 1.24 (d, *J* = 3.1 Hz, 8H), 1.22 (s, 1H), 1.20 (d, *J* = 4.5 Hz, 1H), 1.19 (s, 3H), 1.17 (dd, *J* = 7.0, 4.6 Hz, 2H), 1.10 (s, 3H), 1.10 (s, 3H), 1.07 (d, *J* = 3.6 Hz, 1H), 1.06 (t, *J* = 2.5 Hz, 1H), 1.04 (d, *J* = 4.7 Hz, 1H), 1.02 (d, *J* = 7.0 Hz, 1H), 0.96 (d, *J* = 6.7 Hz, 1H), 0.92 – 0.90 (m, 13H), 0.89 (s, 9H), 0.89 (s, 21H), 0.07 (s, 3H), 0.05 (d, *J* = 1.7 Hz, 15H), 0.05 (s, 3H), 0.03 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 208.86, 208.38, 188.89, 188.16, 141.07, 127.17, 127.02, 120.05, 87.41, 86.47, 80.33, 80.07, 78.89, 78.41, 72.40, 72.38, 70.07, 69.90, 61.07, 60.84, 53.25, 52.76, 48.45, 48.18, 42.66, 37.72, 37.64, 37.12, 34.64, 34.58, 32.13, 32.10, 32.02, 29.85, 29.83, 29.80, 29.15, 29.09, 28.69, 28.65, 28.63, 28.59, 26.06, 26.03, 25.90, 25.39, 25.33, 22.46, 19.46, 18.90, 18.40, 18.14, 18.04, 14.28, 13.33, 12.97, -3.50, -3.86, -4.20, -4.47, -4.59, -4.72.
FTIR (NaCl, thin film, cm^{-1}): 3439, 2949, 2927, 2853, 1694, 1471, 1462, 1374, 1252, 1092 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{39}H_{67}O_4Si_2$: 655.4578 $[M+H]^+$; found: 655.4552.
$[\alpha]_D^{21}$: +42° (*c* = 0.250, $CHCl_3$).

Preparation of allylic alcohol 5:

A 500 mL round-bottom flask with a stir bar was charged with enone **S14** (1.82 g, 2.78 mmol, 1.0 equiv) and CH_2Cl_2 (140 mL, 0.02 M). The resulting solution was cooled to 0 °C and stirred at this temperature for 15 min. Thereafter, *i*-Bu_2AlH (1.0 M in CH_2Cl_2, 8.34 mL, 8.34 mmol, 3.0 equiv) was added dropwise. After stirring at 0 °C for 30 min, the reaction was diluted with Et_2O (100 mL), quenched with st. Na/K-tartrate aq. (100 mL) and vigorously stirred at room temperature for 1 h. The layers were separated. The aqueous layer was further extracted with Et_2O (3 × 50 mL), combined organic layers were washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (20 to 30 to 40% EtOAc/hexanes) to afford allylic alcohol **5** (1.35 g, 2.06 mmol, 1:1 mixture of diastereomers at C20, 74% yield) as a colorless foam.

TLC (25% EtOAc/hexanes): R_f = 0.29 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (t, *J* = 2.4 Hz, 1H), 5.48 (t, *J* = 2.3 Hz, 1H), 5.37 (dt, *J* = 4.0, 1.7 Hz, 2H), 4.85 (dd, *J* = 6.9, 2.5 Hz, 1H), 4.81 (dd, *J* = 6.5, 2.7 Hz, 1H), 3.47 (tt, *J* = 5.1, 4.7 Hz, 2H), 3.23 (ddd, *J* = 10.6, 8.4, 5.8 Hz, 3H), 3.10 – 3.02 (m, 1H), 2.34 (d, *J* = 2.4 Hz, 2H), 2.32 (d, *J* = 2.2 Hz, 2H), 2.27 – 2.23 (m, 3H), 2.23 – 2.19 (m, 3H), 2.19 – 2.14 (m, 2H), 2.08 (dd, *J* = 6.9, 4.4 Hz, 1H), 1.98 – 1.87 (m, 2H), 1.78 (d, *J* = 3.7 Hz, 1H), 1.75 (dd, *J* = 5.1, 2.9 Hz, 2H), 1.73 – 1.71 (m, 2H), 1.64 – 1.61 (m, 1H), 1.61 – 1.60 (m, 1H), 1.59 (s, 1H), 1.58 (s, 1H), 1.57 – 1.55 (m, 2H), 1.53 (q, *J* = 2.4 Hz, 1H), 1.52 – 1.48 (m, 1H), 1.44 (d, *J* = 7.1 Hz, 3H), 1.41 (d, *J* = 7.2 Hz, 3H), 1.33 – 1.29 (m, 2H), 1.28 – 1.26 (m, 12H), 1.25 (s, 6H), 1.04 (s, 3H), 1.03 (s, 3H), 1.02 (s, 1H), 0.99 (dd, *J* = 7.8, 3.1 Hz, 2H), 0.97 (q, *J* = 5.6 Hz, 3H), 0.91 (s, 9H), 0.91 (s, 9H), 0.89 (s, 18H), 0.09 (s, 3H), 0.05 (d, *J* = 1.7 Hz, 15H), 0.05 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.33, 159.45, 155.87, 155.03, 140.82, 140.80, 125.73, 123.98, 121.10, 121.06, 89.60, 88.74, 81.86, 81.36, 76.29, 75.97, 72.63, 72.58, 70.08, 70.07, 59.32, 58.83, 56.79, 54.14, 50.11, 48.88, 42.80, 42.73, 37.79, 37.77, 37.24, 37.20, 34.79, 34.74, 32.13, 32.08, 31.72, 31.64, 30.79, 30.33, 29.86, 29.52, 28.93, 28.89, 28.80, 28.68, 28.63, 26.22, 26.20, 26.08, 26.04, 24.88, 22.85, 19.64, 19.35, 18.42, 18.35, 18.29, 14.28, 13.92, 13.20, 1.17, -3.33, -3.63, -3.75, -4.01, -4.26, -4.44.
FTIR (NaCl, thin film, cm^{-1}): 3383, 2957, 1930, 2856, 1714, 1470, 1463, 1372, 1256, 1090 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{39}H_{67}O_4Si_2$: 655.4578 $[M+H–H_2]^+$; found: 655.4571.
$[\alpha]_D^{21}$: +12° (c = 0.083, CH_2Cl_2).

Preparation of spiroketal 20:

A 250 mL round-bottom flask with a stir bar was charged with Ph_3PAuCl (98.9 mg, 0.20 mmol, 10 mol %), $AgBF_4$ (19.5 mg, 0.1 mmol, 5.0 mol %) and $(CH_2Cl)_2$ (65 mL, 0.03 M total) and stirred at room temperature for 10 min. Allylic alcohol **5** (1.30 g, 1.98 mmol, 1.0 equiv) in $(CH_2Cl)_2$ (5 mL, 0.03 M total) was added. After stirring for 20 h, Et_3N•3HF (6.33 mL, 39.6 mmol, 20 equiv) was added dropwise and stirred for 5 h at room temperature. The reaction was passed through a short pad of SiO_2 using 50% EtOAc/hexanes as the eluent, diluted with st. $NaHCO_3$ aq. (50 mL) and H_2O (50 mL). The layers were separated. The aqueous layer was further extracted with EtOAc (3 × 50 mL), combined organic layers were washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (20 to 25 to 30% EtOAc/hexanes) to afford spiroketal **20** (911 mg, 1.68 mmol, 85% yield) as a colorless foam.

TLC (20% EtOAc/hexanes): R_f = 0.22 (p-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.43 – 5.36 (m, 2H), 4.89 (dd, J = 8.2, 2.3 Hz, 1H), 3.51 (tt, J = 11.1, 4.7 Hz, 1H), 3.22 (dd, J = 10.6, 5.0 Hz, 1H), 2.47 (t, J = 8.2 Hz, 1H), 2.33 (ddd, J = 13.0, 5.1, 2.2 Hz, 1H), 2.25 (dt, J = 11.0, 2.3 Hz, 1H), 2.21 – 2.11 (m, 2H), 2.09 (td, J = 4.9, 2.4 Hz, 1H), 2.06 – 1.98 (m, 4H), 1.97 – 1.91 (m, 1H), 1.89 – 1.83 (m, 1H), 1.79 (dt, J = 13.1, 3.4 Hz, 1H), 1.69 (dd, J = 6.2, 3.8 Hz, 1H), 1.67 – 1.64 (m, 1H), 1.63 (dd, J = 10.2, 2.0 Hz, 1H), 1.59 – 1.57 (m, 1H), 1.54 – 1.48 (m, 1H), 1.36 (s, 3H), 1.17 (s, 3H), 1.10 (d, J = 3.3 Hz, 1H), 1.06 (s, 3H), 1.05 – 1.02 (m, 1H), 1.02 – 0.97 (m, 6H), 0.96 (d, J = 6.5 Hz, 1H), 0.91 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.02, 139.98, 121.54, 120.63, 117.51, 84.31, 81.98, 79.62, 71.76, 55.96, 53.61, 49.16, 42.25, 41.86, 37.48, 37.29, 37.13, 33.63, 31.64, 30.73, 30.33, 30.12, 29.08, 28.60, 26.13, 19.37, 18.20, 14.49, 13.88, -3.61, -4.05.
FTIR (NaCl, thin film, cm^{-1}): 3392, 2957, 2930, 2857, 1471, 1462, 1373, 1251, 1099, 1070 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{33}H_{55}O_4Si$: 543.3870 $[M+H]^+$; found: 543.3893.
$[\alpha]_D^{21}$: –67° (c = 0.167, $CHCl_3$).

Minimized Structures and energies:

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Single-point energy = -2406.101814191406 (Hartree)
N_atoms = 113

C	-4.2612945	3.1439595	3.605928
C	-3.1775145	2.161998	3.6497575
C	-2.338009	2.237628	2.4354575
C	-1.126178	2.968367	2.8920965
C	-0.037664	2.0969355	2.5738055
C	-0.4030685	1.035947	1.9668315
C	0.4228185	0.038453	1.350371
C	1.851007	0.2410315	1.577091
C	2.665246	-0.56034	0.721119
C	2.2599615	-1.1731	-0.321583
C	3.177214	-1.9667585	-1.1022185
C	3.162845	-1.604117	-2.52126
O	3.9388865	-2.449306	-3.2554915
Si	5.498797	-2.3265755	-3.601855
C	5.948927	-0.6085685	-3.9029365
C	6.507916	-2.9591545	-2.251198
C	5.7003365	-3.349371	-5.100168
C	4.913206	-2.7767915	-6.202072
C	7.115439	-3.397334	-5.4962875
C	5.2272305	-4.716723	-4.8364805
C	1.802126	-1.673919	-3.0297045
C	0.895728	-0.8317675	-2.2519365
C	0.879103	-1.1122685	-0.7921685
C	0.233898	-2.419202	-0.5490745
C	0.145802	-0.001614	-0.1075965
C	-1.2964885	0.0118315	-0.397269
C	-2.0391985	1.06258	0.3019835
O	-3.3672285	0.969084	-0.001853
Si	-4.156109	1.752503	-1.1604735
C	-4.154989	3.5223545	-0.828051
C	-3.391661	1.4974415	-2.772778
C	-5.8360395	1.0440185	-1.1016395
C	-6.441669	1.2780045	0.217749
C	-6.6797145	1.6665245	-2.1331015
C	-5.768712	-0.4049455	-1.3417285
C	-1.8455	0.982835	1.773467
C	-2.4439085	-0.250586	2.296286
O	-1.266547	3.235874	4.2289665
C	-2.2433055	2.421503	4.763641
C	-1.6318575	1.2687905	5.4323115
C	-1.155484	1.8676815	6.6755045
C	-2.1643135	2.907296	6.9664445
C	-1.567475	4.181009	7.3447035
C	-3.1626765	2.4701245	7.9341685
O	-2.840873	3.0931115	5.758497

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H	-3.599564	1.2204305	3.7674535
H	-2.851029	2.7934	1.724306
H	-1.003927	3.899228	2.433875
H	0.9351425	2.3586905	2.796967
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H	2.084343	0.04763	2.5765835
H	2.091115	1.248897	1.4282495
H	3.6665	-0.631848	0.980413
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H	5.359258	-0.1718285	-4.641085
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H	-3.1841275	3.900505	-0.81366
H	-3.9215535	1.9995125	-3.5164305
H	-3.351356	0.491718	-3.036678
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H	-5.8759075	0.852813	0.9806505
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H	-6.3038965	1.514976	-3.0930615

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H -0.935361 4.510628 6.588847
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H -2.7465385 2.386969 8.8853545
H -3.944365 3.15533 7.9786565

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Single-point energy = -2406.095200694148 (Hartree)
N_atoms = 113
C 4.165177 3.0501625 1.713936
C 3.3047445 2.409058 2.7093075
C 2.1830125 1.5466105 2.235926
C 1.0977405 2.531394 2.0246775
C 0.934933 2.5771555 0.60687
C 1.518736 1.598232 0.0272995
C 1.3351735 1.1141125 -1.307094
C 0.677097 2.062186 -2.2000875
C 0.213455 1.45139 -3.4041515
C 0.0897705 0.1959845 -3.5930085
C -0.382162 -0.3063675 -4.859688
C -1.5199385 -1.2140155 -4.714311
O -1.83117 -1.7220925 -5.941544
Si -3.277002 -1.9114975 -6.607187
C -3.0118195 -3.1727675 -7.8537835
C -4.4705165 -2.4948565 -5.3899765
C -3.853194 -0.346217 -7.367844
C -5.15604 -0.555103 -8.0181545
C -2.881669 0.1035305 -8.375003
C -4.001034 0.7028065 -6.3483205
C -1.1770745 -2.2849475 -3.7886385
C -0.7502655 -1.747106 -2.4974415
C 0.393527 -0.799501 -2.56763
C 1.61898 -1.527351 -2.955478
C 0.542996 -0.1432985 -1.23022
C 1.0425765 -1.0552435 -0.1857525
C 1.3193565 -0.4342975 1.1150865
O 1.8814145 -1.36624 1.940363
Si 1.1637395 -2.1586965 3.137516

C	-0.168945	-3.1988955	2.513372
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C	3.6051505	-2.278235	4.292818
C	3.0326525	-4.0906515	2.8446695
C	2.0212995	-3.9237055	5.0105655
C	2.2185295	0.7470215	0.9795305
C	3.552609	0.306752	0.553624
O	1.498343	3.720257	2.594294
C	2.529238	3.424166	3.4400755
C	3.129114	4.6782045	3.8691695
C	2.2245685	5.107771	4.934098
C	1.720437	3.842531	5.5136085
C	0.2688195	3.8323085	5.6486895
C	2.3780685	3.499745	6.768162
O	2.084254	2.8579195	4.597344
H	4.8292765	2.3760075	1.291559
H	4.738239	3.7949275	2.1613515
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H	3.8965665	1.88304	3.384562
H	1.956314	0.9195845	3.029925
H	0.202928	2.2480255	2.487883
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H	1.3247715	2.8507205	-2.4215785
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H	-0.047243	2.095925	-4.173087
H	0.3650825	-0.847205	-5.3508105
H	-0.6383655	0.4840945	-5.4867795
H	-2.3289825	-0.677162	-4.3226655
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H	-2.7549145	-4.075907	-7.4039465
H	-3.863049	-3.3373845	-8.430687
H	-5.4004875	-2.662843	-5.828346
H	-4.61421	-1.8193755	-4.610655
H	-4.156931	-3.3954845	-4.971456
H	-5.89116	-0.846697	-7.3397065
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H	-5.112386	-1.276808	-8.768593
H	-2.7790195	-0.5839845	-9.1509985
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H	-3.1879675	1.0070815	-8.801774
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H	-3.097942	0.9203335	-5.877459
H	-4.6901845	0.4407325	-5.611719
H	-0.425762	-2.863675	-4.221853
H	-1.998064	-2.912836	-3.6545885
H	-1.558779	-1.246481	-2.065037
H	-0.511839	-2.533644	-1.8573405
H	1.762073	-2.3735705	-2.367685
H	1.5782045	-1.8440925	-3.943909

H	2.4611755	-0.9228625	-2.865755
H	-0.417521	0.158847	-0.946046
H	0.3554715	-1.821242	-0.0271155
H	1.9183685	-1.5202885	-0.496489
H	0.420139	-0.090288	1.525379
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H	1.1669925	-0.3805765	4.7519705
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H	3.299193	-1.6042275	5.0265325
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H	3.8275665	-4.6435005	3.237659
H	3.3824895	-3.5855545	2.004807
H	2.308498	-4.771177	2.5311465
H	1.6675595	-3.305478	5.7711555
H	1.2549685	-4.5817405	4.753097
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H	3.511798	-0.459547	-0.14653
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H	4.0917335	-0.0548525	1.3650065
H	3.2054535	5.3632625	3.0936505
H	4.083182	4.4910825	4.242628
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H	-0.0482465	4.56342	6.320653
H	2.120763	2.53511	7.0616985
H	3.413302	3.539654	6.6681905
H	2.0969515	4.156803	7.5260445

Preparation of C3 alcohol S15:

A 100 mL round-bottom flask with a stir bar was charged with spiroketal **20** (147 mg, 0.27 mmol, 1.0 equiv) and adventitious water was removed via azeotropic drying with PhMe (3 x 10 mL) under high vacuum. Thereafter, *i*-PrOH (freshly distilled over CaH_2, 10.8 mL, 0.025 M), $PhSiH_3$ (200 µL, 1.62 mmol, 6.0 equiv), and TBHP solution (5.5 M in nonane, 197 µL, 1.08 mmol, 4.0 equiv) were added. The mixture was subjected to three freeze-pump-thaw cycles. Thereafter, $Mn(dpm)_3$ (82 mg, 0.135 mmol, 50 mol %) was added in one portion. After stirring at room temperature for 6 h, the reaction was passed through a short

pad of SiO_2 using 50% EtOAc/hexanes as the eluent and concentrated in vacuo. The crude product was purified by flash column chromatography (15 to 25 to 35% EtOAc/hexanes) to afford C3 alcohol **S15** (<147 mg, <0.27 mmol, <100 % yield) as a colorless foam.[8] This material contained an excess $PhSiH_3$ and could be carried through the next step where a two-step yield was recorded. It could be exhaustively purified by multiple rounds of chromatography for analytical characterization.

TLC (20% EtOAc/hexanes): R_f = 0.25 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.45 (t, *J* = 6.9 Hz, 1H), 3.58 (tt, *J* = 11.0, 4.7 Hz, 1H), 3.29 (dd, *J* = 11.5, 4.5 Hz, 1H), 2.40 (dd, *J* = 9.2, 7.4 Hz, 1H), 2.01 – 1.96 (m, 1H), 1.96 – 1.87 (m, 3H), 1.86 – 1.73 (m, 4H), 1.73 – 1.70 (m, 1H), 1.70 – 1.68 (m, 1H), 1.67 (d, *J* = 1.7 Hz, 1H), 1.66 – 1.61 (m, 2H), 1.57 – 1.54 (m, 2H), 1.50 (dd, *J* = 12.7, 3.5 Hz, 2H), 1.46 – 1.40 (m, 1H), 1.40 – 1.36 (m, 1H), 1.32 (s, 3H), 1.30 (d, *J* = 6.4 Hz, 1H), 1.28 (dd, *J* = 6.8, 2.3 Hz, 2H), 1.26 – 1.22 (m, 3H), 1.20 (d, *J* = 2.1 Hz, 1H), 1.14 (s, 3H), 1.10 – 1.03 (m, 2H), 1.01 (t, *J* = 3.9 Hz, 1H), 0.99 – 0.96 (m, 1H), 0.96 – 0.91 (m, 5H), 0.89 (d, *J* = 3.3 Hz, 14H), 0.80 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 116.66, 81.72, 79.61, 73.97, 71.47, 56.96, 48.70, 47.61, 45.52, 44.54, 41.93, 38.25, 37.50, 37.07, 35.51, 33.37, 32.56, 32.46, 32.07, 31.48, 30.56, 30.20, 29.00, 28.63, 26.11, 18.21, 14.50, 13.69, 12.33, -3.26, -4.65.
FTIR (NaCl, thin film, cm^{-1}): 3398, 2926, 2858, 1470, 1462, 1455, 1382, 1366, 1255, 1085 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{33}H_{59}O_4Si$: 547.4183 $[M+H]^+$; found: 547.4181.
$[\alpha]_D^{21}$: –39° (*c* = 0.417, $CHCl_3$).

Figure S1. DFT thermodynamic study for stereochemical outcomes of western and eastern C14–C15 alkene reduction

Minimized Structures and energies:

S15a

Single-point energy = -1882.063903502656 (Hartree)
N_atoms = 96
C 3.944346 0.312602 1.635718
C 3.307516 -0.4003555 0.539361

C	1.969351	0.0965405	0.162229
C	1.913441	-0.140255	-1.3051875
C	0.818017	-1.0723625	-1.5609195
C	0.5115085	-1.679696	-0.255265
C	-0.803167	-2.328972	-0.118547
C	-1.000564	-3.367881	-1.1331795
C	-2.3053335	-4.0115085	-1.0236705
C	-3.376423	-3.017425	-1.0604525
C	-4.709759	-3.620338	-1.142073
C	-5.7504075	-2.6129895	-1.3195475
O	-6.9958975	-3.1614765	-1.4100405
C	-5.672072	-1.592395	-0.2797915
C	-4.329621	-1.0143335	-0.1661635
C	-3.2571425	-2.0137195	0.035788
C	-3.415332	-2.6232355	1.3660945
C	-1.916405	-1.3584655	-0.0993295
C	-1.654359	-0.3157245	0.9022815
C	-0.3695275	0.3499545	0.6980205
O	-0.1524575	1.31983	1.633433
Si	-0.8056265	2.7625325	1.8804815
C	0.3526705	3.5221375	3.020832
C	-2.40027	2.6107335	2.7076945
C	-0.9769805	3.766546	0.351296
C	-1.323271	5.1447445	0.7401295
C	-2.043638	3.253464	-0.5209805
C	0.2863275	3.797662	-0.39945
C	0.776538	-0.5950615	0.728516
C	0.973571	-1.105086	2.084945
O	3.1066795	-0.7335845	-1.647204
C	4.0425055	-0.3553445	-0.7328265
C	5.217442	-1.2211035	-0.9083805
C	6.294254	-0.3244075	-1.3409265
C	5.602576	0.9116635	-1.747775
C	5.2159765	0.8949055	-3.1589645
C	6.340157	2.120509	-1.419949
O	4.47055	0.9175075	-0.948791
H	4.8918185	-0.0717345	1.8398205
H	4.054853	1.317962	1.3990485
H	3.3831535	0.237814	2.5078035
H	3.243239	-1.4133205	0.78023
H	1.919324	1.110536	0.384199
H	1.816006	0.7456915	-1.847319
H	1.1040865	-1.769905	-2.2766045
H	-0.0027755	-0.559142	-1.9462405
H	1.2289135	-2.422803	-0.09086
H	-0.7930175	-2.8068645	0.8115895
H	-0.235895	-4.075433	-1.0660275
H	-0.9217475	-2.9410185	-2.0829975
H	-2.4344075	-4.691833	-1.8042085
H	-2.3625865	-4.5644815	-0.1402655
H	-3.2470715	-2.475238	-1.9488365

S15a

H -4.7449385 -4.292837 -1.9382685
H -4.9110385 -4.1787525 -0.2805445
H -5.6104955 -2.1545175 -2.247821
H -7.158658 -3.5788125 -0.6015195
H -5.9572725 -2.0202245 0.6307885
H -6.368916 -0.8439225 -0.4799665
H -4.328377 -0.3198375 0.610764
H -4.125317 -0.4745325 -1.038241
H -3.4165595 -1.893632 2.1079155
H -2.6575535 -3.2963795 1.595842
H -4.3130495 -3.1391765 1.4539025
H -1.935744 -0.8885485 -1.0357095
H -1.671601 -0.7163825 1.8629795
H -2.4031345 0.4057935 0.8712275
H -0.386264 0.8009835 -0.2450735
H 0.0098585 4.441291 3.369474
H 0.491802 2.903456 3.8467315
H 1.284919 3.6718015 2.583347
H -2.3023655 2.0202105 3.5600225
H -3.1341675 2.1787385 2.1099545
H -2.7542425 3.5422955 3.012745
H -1.4437575 5.740012 -0.110387
H -0.580194 5.585605 1.3211465
H -2.217193 5.192658 1.273684
H -2.966212 3.226555 -0.0381345
H -2.154418 3.86721 -1.359848
H -1.843366 2.293627 -0.8726485
H 0.5711675 2.8529575 -0.731216
H 1.0704655 4.178204 0.1710655
H 0.1918515 4.408824 -1.2418265
H 0.138821 -1.622803 2.4276005
H 1.774363 -1.7671955 2.1250255
H 1.149023 -0.3290195 2.7518925
H 5.454262 -1.712358 -0.023205
H 4.9899995 -1.94389 -1.6187815
H 6.939299 -0.119452 -0.549741
H 6.8644865 -0.724375 -2.113465
H 4.631229 1.72754 -3.376963
H 4.6596235 0.046946 -3.3816155
H 6.0582975 0.9177375 -3.7720445
H 7.231908 2.16526 -1.955958
H 5.780846 2.9664135 -1.653188
H 6.5635645 2.14666 -0.404464

S15b

Single-point energy = -1882.0604906961223 (Hartree)
N_atoms = 96
C 3.5722425 1.118087 1.4307455
C 2.952779 -0.1684775 1.1421925
C 2.074434 -0.176138 -0.0466905

C	2.6422945	-1.2551875	-0.8963405
C	1.5305195	-1.957912	-1.53796
C	0.391969	-1.0642045	-1.303132
C	-0.963165	-1.5485285	-1.5538325
C	-1.1134325	-2.102343	-2.9015645
C	-2.4972815	-2.4472585	-3.213877
C	-3.3855865	-1.306962	-3.0003935
C	-4.752695	-1.551732	-3.468103
C	-5.572809	-0.3470265	-3.3854935
O	-6.8421005	-0.5468435	-3.8416765
C	-5.5502265	0.202599	-2.034588
C	-4.184652	0.413586	-1.5453305
C	-3.3302465	-0.793485	-1.600991
C	-3.821672	-1.775848	-0.6225175
C	-1.9061645	-0.4290655	-1.3224595
C	-1.6819995	0.1805835	-0.0021315
C	-0.2957165	0.602557	0.2384105
O	-0.191551	1.134971	1.493911
Si	-0.2180235	2.659803	1.9929805
C	0.638165	3.728582	0.8219565
C	0.664457	2.5957165	3.555619
C	-1.914292	3.3130315	2.2857885
C	-2.7376265	2.3093695	2.9740575
C	-1.816745	4.5088725	3.141301
C	-2.574006	3.7091735	1.033025
C	0.628142	-0.531886	0.0686935
C	0.4134865	-1.541518	1.114901
O	3.313373	-2.0739425	-0.0231905
C	3.9327675	-1.249965	0.8733455
C	4.39893	-2.057566	1.989582
C	5.6610885	-2.600665	1.4932725
C	6.1482305	-1.5754445	0.542301
C	6.52762	-2.148384	-0.7431065
C	7.216124	-0.751898	1.095119
O	5.063463	-0.7222825	0.3401485
H	2.8487215	1.827705	1.660521
H	4.219029	1.051997	2.24449
H	4.1269075	1.458895	0.621165
H	2.407685	-0.4638755	1.976757
H	2.1435265	0.7366545	-0.546516
H	3.3228045	-0.8729375	-1.588984
H	1.393034	-2.883051	-1.080305
H	1.7032765	-2.1309035	-2.5486245
H	0.5272055	-0.2460775	-1.9463195
H	-1.171694	-2.312882	-0.87365
H	-0.502002	-2.9392445	-3.013498
H	-0.776434	-1.397199	-3.597467
H	-2.567375	-2.75951	-4.207298
H	-2.8066845	-3.259257	-2.634604
H	-3.008309	-0.529247	-3.594474
H	-4.735727	-1.886766	-4.455404

S15b

H	-5.2000925	-2.312752	-2.907023
H	-5.1784265	0.364612	-4.040687
H	-7.2250165	-1.17965	-3.2873265
H	-6.078497	1.1007745	-2.0179755
H	-6.06339	-0.4499315	-1.398691
H	-3.7384465	1.164061	-2.120789
H	-4.229812	0.780255	-0.571422
H	-3.2158345	-2.617847	-0.5554155
H	-4.778788	-2.1125805	-0.848506
H	-3.868412	-1.353455	0.327448
H	-1.662188	0.299177	-2.0369295
H	-1.946957	-0.482376	0.7552895
H	-2.2933075	1.0130665	0.1112715
H	-0.0339425	1.3293425	-0.4692355
H	0.6282505	4.7163425	1.153779
H	0.1987725	3.717756	-0.121837
H	1.633979	3.4486105	0.7085145
H	0.8153305	3.5457725	3.953401
H	0.1426185	2.036359	4.261951
H	1.59652	2.151314	3.4324155
H	-3.6848365	2.6964745	3.187111
H	-2.8673855	1.452331	2.3988925
H	-2.3142525	2.016396	3.8801035
H	-1.223611	5.2525905	2.714623
H	-2.7651	4.9220325	3.288575
H	-1.4263455	4.29111	4.081263
H	-2.684157	2.9132125	0.3710745
H	-2.0486975	4.4598185	0.5378385
H	-3.5315085	4.0794225	1.2284365
H	-0.493894	-2.037716	1.0121505
H	1.164511	-2.2578245	1.1010615
H	0.4077855	-1.0890165	2.0501415
H	3.7079565	-2.7866765	2.2535695
H	4.5520975	-1.43972	2.81409
H	6.34852	-2.780232	2.252973
H	5.493048	-3.500268	0.99924
H	5.73072	-2.682459	-1.1426645
H	6.7939545	-1.3996465	-1.41537
H	7.341181	-2.791204	-0.636214
H	7.4259345	0.0407435	0.4547385
H	6.940649	-0.3562405	2.0173865
H	8.0870205	-1.3086895	1.222976

Preparation of ketone 3:

A 100 mL round-bottom flask with a stir bar was charged with C3 alcohol **S15** (<147 mg, <0.27 mmol, 1.0 equiv), $Cu(MeCN)_4OTf$ (10.1 mg, 0.027 mmol, 10 mol %), ^{MeO}bpy (5.84 mg, 0.027 mmol, 10 mol %), ABNO (3.79 mg, 0.027 mmol, 10 mol %), NMI (4.30 µL, 0.054 mmol, 20 mol %) and MeCN/THF (3:1, 18.0 mL, 0.015 M). The resulting solution was sparged with O_2 for 5 min, then vigurously stirred (1200 rpm) at room temperature under O_2 atmosphere for 12 h. The reaction was passed through a short pad of SiO_2 using 50% EtOAc/hexanes as the eluent and concentrated in vacuo. The crude product was purified by flash column chromatography (10 to 15 to 20% EtOAc/hexanes) to afford eastern fragment ketone **3** (112 mg, 0.21 mmol, 76% yield over 2 steps) as a colorless foam.

TLC (20% EtOAc/hexanes): R_f = 0.42 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.45 (t, *J* = 6.9 Hz, 1H), 3.32 (dd, *J* = 11.4, 4.5 Hz, 1H), 2.44 – 2.35 (m, 2H), 2.34 – 2.31 (m, 1H), 2.30 – 2.21 (m, 1H), 2.10 (ddd, *J* = 15.2, 4.1, 2.1 Hz, 1H), 2.00 (ddt, *J* = 5.7, 4.1, 2.0 Hz, 1H), 1.98 – 1.96 (m, 1H), 1.96 – 1.88 (m, 3H), 1.85 (td, *J* = 7.9, 3.8 Hz, 1H), 1.80 – 1.75 (m, 1H), 1.69 (dd, *J* = 4.2, 3.1 Hz, 1H), 1.68 – 1.63 (m, 2H), 1.59 (d, *J* = 3.0 Hz, 1H), 1.58 – 1.52 (m, 3H), 1.50 – 1.42 (m, 1H), 1.37 (d, *J* = 4.1 Hz, 1H), 1.35 (s, 1H), 1.32 (d, *J* = 4.5 Hz, 5H), 1.30 – 1.24 (m, 2H), 1.14 (s, 3H), 1.12 (d, *J* = 6.4 Hz, 1H), 1.10 – 1.04 (m, 2H), 1.00 (s, 3H), 0.96 – 0.93 (m, 4H), 0.92 (s, 3H), 0.90 (d, *J* = 1.5 Hz, 10H), 0.05 (s, 3H), 0.02 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 211.90, 116.62, 81.75, 79.46, 73.72, 56.95, 48.74, 47.46, 46.26, 45.11, 44.72, 41.94, 38.42, 38.14, 37.50, 35.66, 33.35, 32.46, 32.42, 31.71, 30.70, 30.19, 29.23, 28.64, 26.09, 18.20, 14.49, 13.67, 11.50, -3.26, -4.63.
FTIR (NaCl, thin film, cm^{-1}): 2955, 2931, 2857, 1715, 1462, 1252, 1116, 1088, 1004, 836 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{33}H_{57}O_4Si$: 545.4026 $[M+H]^+$; found: 545.4041.
$[\alpha]_D^{21}$: –21° (*c* = 0.133, $CHCl_3$).

Preparation of α-bromo ketone S16:

In an N_2-filled glovebox, a 50 mL round-bottom flask with a stir bar was charged with ketone **3** (80 mg, 0.15 mmol) and THF (7.5 mL, 0.01 M total). The flask was removed from the glovebox and the resulting solution was cooled to 0 °C and stirred at this temperature for 5 min. A solution of $PhNMe_3Br_3$ (62 mg, 0.165 mmol, 1.1 equiv) in THF (7.5 mL, 0.01 M total) was also cooled to 0 °C, added by cannula, and the reaction stirred at 0 °C for 30 min. The reaction was quenched with st. $Na_2S_2O_3$ aq. (7.5 mL) and H_2O (7.5mL) and was diluted with hexane (7.5 mL). The layers were separated. The aqueous layer was further extracted with hexane (3 × 7.5 mL), combined organic layers were washed with brine (1 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column

chromatography (10 to 15 to 20% EtOAc/hexanes) to afford α-bromo ketone **S16** (78.5 mg, 0.13 mmol, 84% yield) as an off-yellow foam.[7]

TLC (15% EtOAc/hexanes): R_f = 0.27 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74 (dd, *J* = 13.3, 6.2 Hz, 1H), 4.49 – 4.41 (m, 1H), 3.31 (dd, *J* = 11.3, 4.5 Hz, 1H), 2.58 (dd, *J* = 12.8, 6.3 Hz, 1H), 2.45 – 2.38 (m, 3H), 2.01 – 1.96 (m, 1H), 1.96 – 1.91 (m, 2H), 1.89 – 1.81 (m, 2H), 1.78 (dd, *J* = 9.2, 3.2 Hz, 1H), 1.75 – 1.70 (m, 1H), 1.70 – 1.64 (m, 2H), 1.63 (dd, *J* = 6.6, 1.6 Hz, 1H), 1.59 (s, 1H), 1.57 (s, 1H), 1.55 – 1.49 (m, 2H), 1.43 – 1.38 (m, 1H), 1.38 – 1.36 (m, 1H), 1.34 (d, *J* = 8.7 Hz, 1H), 1.32 (s, 3H), 1.31 – 1.28 (m, 1H), 1.28 – 1.24 (m, 2H), 1.21 (d, *J* = 11.2 Hz, 1H), 1.19 – 1.15 (m, 1H), 1.14 (s, 3H), 1.13 – 1.09 (m, 1H), 1.08 (s, 3H), 1.02 – 0.96 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 4H), 0.92 (s, 3H), 0.90 (s, 10H), 0.06 (s, 3H), 0.04 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.03, 116.59, 81.78, 79.32, 73.42, 56.90, 54.28, 51.46, 48.73, 47.29, 47.06, 44.89, 43.95, 41.92, 38.99, 37.49, 33.31, 32.37, 32.02, 31.51, 30.71, 30.19, 28.70, 28.63, 26.08, 18.18, 14.48, 13.69, 12.14, -3.19, -4.64.
FTIR (NaCl, thin film, cm^{-1}): 2954, 2930, 2857, 1731, 1462, 1456, 1363, 1253, 1185, 1089 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{33}H_{56}O_4SiBr$: 623.3131 $[M+H]^+$; found: 623.3108.
$[\alpha]_D^{21}$: –0.22° (*c* = 0.208, $CHCl_3$).

Preparation of α-azido ketone S17:

In an N_2-filled glovebox, a 25 mL round-bottom flask with a stir bar was charged with α-bromo ketone **S16** (31 mg, 0.05 mmol, 1.0 equiv) and *n*-$PrNO_2$ (5.0 mL, 0.01 M). $TMGN_3$ (31.4 mg, 0.20 mmol, 4.0 equiv) was added, and the reaction was stirred at room temperature for 4 h. Upon completion, the reaction was diluted with heptane (5 mL) and was concentrated in vacuo. The crude material was azeotroped with another 5 mL of heptane to remove *n*-$PrNO_2$. The crude product was purified by flash column chromatography (5 to 10 to 15 to 20 to 25% EtOAc/hexanes) to afford α-azido ketone **S17** (19.7 mg, 0.034 mmol, 68% yield) as a colorless foam.[7]

TLC (20% EtOAc/hexanes): R_f = 0.52 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.45 (t, *J* = 6.1 Hz, 1H), 3.98 (dd, *J* = 13.1, 6.3 Hz, 1H), 3.32 (dd, *J* = 11.3, 4.5 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.38 – 2.32 (m, 1H), 2.28 (d, *J* = 4.0 Hz, 1H), 2.27 – 2.25 (m, 1H), 2.25 – 2.21 (m, 1H), 2.00 – 1.96 (m, 1H), 1.95 (s, 1H), 1.94 (d, *J* = 1.7 Hz, 1H), 1.92 (d, *J* = 1.7 Hz, 1H), 1.89 (dd, *J* = 7.3, 5.3 Hz, 1H), 1.86 – 1.82 (m, 1H), 1.77 (dq, *J* = 9.4, 6.7 Hz, 2H), 1.70 (d, *J* = 4.4 Hz, 1H), 1.67 (t, *J* = 1.7 Hz, 1H), 1.66 – 1.62 (m, 2H), 1.59 (s, 1H), 1.56 (s, 1H), 1.54 (d, *J* = 4.0 Hz, 1H), 1.52 (d, *J* = 4.0 Hz, 1H), 1.51 – 1.47 (m, 1H), 1.44 – 1.40 (m, 1H), 1.39 (s, 1H), 1.38 (d, *J* = 1.8 Hz, 1H), 1.36 (s, 1H), 1.34 – 1.33 (m, 1H), 1.32 (s, 3H), 1.30 (d, *J* = 1.7 Hz, 1H), 1.28 (d, *J* = 4.0 Hz, 1H), 1.25 (s, 3H), 1.20 – 1.17 (m, 1H), 1.14 (s, 4H), 1.13 – 1.10 (m, 1H), 1.08 (s, 4H), 0.94 (d, *J* = 6.6 Hz, 4H), 0.92 (s, 3H), 0.90 (s, 10H), 0.88 (d, *J* = 1.6 Hz, 1H), 0.87 – 0.82 (m, 2H), 0.06 (s, 3H), 0.03 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 205.11, 116.60, 81.79, 79.34, 73.45, 63.81, 56.92, 48.74, 47.31, 47.17, 45.26, 44.93, 43.79, 41.93, 37.49, 36.93, 33.32, 32.37, 31.95, 31.56, 30.77, 30.19, 29.85, 28.71, 28.63, 26.08, 18.19, 14.48, 13.69, 12.53, -3.19, -4.64.
FTIR (NaCl, thin film, cm^{-1}): 2924, 2858, 2103, 1728, 1557, 1462, 1456, 1363, 1258, 1090 cm^{-1}.

HRMS (FAB+, m/z): calc'd for $C_{33}H_{56}N_3O_4Si$: 586.4040 $[M+H]^+$; found: 586.4060.
$[\alpha]_D^{21}$: +21° (c = 0.250, $CHCl_3$).

Preparation of α-azido methoxime S18:

A 10 mL round-bottom flask with a stir bar was charged with α-azido ketone **S17** (16.0 mg, 0.027 mmol) and CH_2Cl_2/py. (14:1, 2.7 mL, 0.01 M). $MeONH_2$•HCl (6.84 mg, 0.082 mmol, 3.0 equiv) was added, and the reaction was stirred at room temperature for 2 h, then concentrated in vacuo. The crude product was purified by flash column chromatography (5 to 10 to 15% EtOAc/hexanes) to afford α-azido methoxime **S18** (16.6 mg, 0.027 mmol, 99% yield) as a colorless foam.[9]

TLC (10% EtOAc/hexanes): R_f = 0.43 (p-anisaldehyde)
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.45 (t, J = 6.8 Hz, 1H), 3.97 (dd, J = 12.0, 5.4 Hz, 1H), 3.90 (s, 3H), 3.31 (dd, J = 11.2, 4.5 Hz, 1H), 3.01 (dd, J = 15.5, 3.3 Hz, 1H), 2.41 (dd, J = 9.2, 7.4 Hz, 1H), 2.17 – 2.11 (m, 1H), 2.01 – 1.93 (m, 2H), 1.93 – 1.89 (m, 1H), 1.88 – 1.80 (m, 1H), 1.79 – 1.74 (m, 1H), 1.73 – 1.68 (m, 1H), 1.67 (t, J = 1.8 Hz, 1H), 1.65 – 1.60 (m, 2H), 1.59 (d, J = 5.0 Hz, 1H), 1.57 – 1.52 (m, 2H), 1.51 (t, J = 3.8 Hz, 1H), 1.45 – 1.39 (m, 1H), 1.32 (s, 3H), 1.31 – 1.29 (m, 1H), 1.27 (s, 1H), 1.26 – 1.23 (m, 3H), 1.20 (d, J = 5.4 Hz, 1H), 1.14 (s, 3H), 1.13 – 1.09 (m, 1H), 1.08 – 1.03 (m, 1H), 0.94 (d, J = 6.6 Hz, 3H), 0.91 (s, 3H), 0.90 (s, 11H), 0.89 – 0.86 (m, 2H), 0.06 (s, 3H), 0.04 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 155.54, 116.62, 81.76, 79.42, 73.62, 62.11, 57.77, 56.94, 48.69, 47.43, 45.10, 44.86, 44.48, 41.93, 37.50, 36.54, 33.34, 32.39, 32.03, 31.58, 30.53, 30.20, 28.64, 28.44, 27.58, 26.10, 18.21, 14.49, 13.71, 12.46, -3.18, -4.62.
FTIR (NaCl, thin film, cm^{-1}): 3146, 2930, 1858, 2106, 1675, 1462, 1455, 1381, 1251, 1088, 1048 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{34}H_{59}N_4O_4Si$: 615.4306 $[M+H]^+$; found: 615.4302.
$[\alpha]_D^{21}$: +14° (c = 0.250, $CHCl_3$).

Preparation of eastern fragment α-amino methoxime 21:

A 10 mL round-bottom flask with a stir bar was charged with α-azido methoxime **S18** (11.0 mg, 0.018 mmol), THF/H_2O (39:1, 1.8 mL, 0.01 M). Ph_3P (18.8 mg, 0.072 mmol, 4.0 equiv) was added, and the reaction was stirred at room temperature for 24 h, then concentrated in vacuo. The crude product was

purified by flash column chromatography (0 to 3 to 7% MeOH/DCM) to afford α-amino methoxime **21** (10.5 mg, 0.018 mmol, quant. yield) as a colorless foam.[9]

Note: The product α-amino methoxime is very sensitive to acidic conditions (e.g. $CDCl_3$, impurity in EtOAc).

TLC (5% MeOH/DCM): R_f = 0.36 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, C_6D_6): δ 4.94 (t, *J* = 7.0 Hz, 1H), 4.38 (s, 1H), 3.99 (s, 3H), 3.47 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.43 – 3.35 (m, 1H), 3.18 (dd, *J* = 14.8, 3.7 Hz, 1H), 2.81 (dd, *J* = 9.4, 7.4 Hz, 1H), 2.26 (dd, *J* = 12.4, 4.8 Hz, 1H), 2.20 – 2.09 (m, 2H), 2.05 – 1.97 (m, 3H), 1.91 (dd, *J* = 13.8, 7.7 Hz, 1H), 1.74 (dt, *J* = 11.6, 5.8 Hz, 2H), 1.65 – 1.57 (m, 2H), 1.55 (s, 3H), 1.46 (d, *J* = 3.0 Hz, 2H), 1.43 – 1.33 (m, 6H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 3H), 1.19 – 1.15 (m, 4H), 1.11 (s, 9H), 1.02 (dt, *J* = 10.1, 3.4 Hz, 2H), 0.99 – 0.94 (m, 1H), 0.94 – 0.87 (m, 3H), 0.66 (s, 3H), 0.39 (s, 1H), 0.20 (s, 3H), 0.18 (s, 3H).
^{13}C NMR (101 MHz, C_6D_6): δ 115.64, 80.43, 78.58, 72.91, 60.26, 56.38, 47.86, 46.52, 44.05, 44.02, 41.19, 36.63, 35.05, 32.37, 31.65, 30.98, 30.62, 29.50, 29.16, 29.04, 27.57, 27.36, 26.47, 25.04, 17.13, 13.68, 12.74, 10.97, 0.22, -4.41, -5.92.
FTIR (NaCl, thin film, cm^{-1}): 3365, 2934, 2858, 1602, 1462, 1456, 1381, 1361, 1251, 1088, 1047 cm^{-1}.
HRMS (FAB+, m/z): calc'd for $C_{34}H_{61}N_2O_4Si$: 589.4401 $[M+H]^+$; found: 589.4404.
$[\alpha]_D^{21}$: +16° (*c* = 0.083, CH_2Cl_2).

2vi. Synthesis of ritterazine B (1)

Preparation of pyrazine S19:

In an N_2-filled glovebox, a 10 mL round-bottom flask with a stir bar equipped with a Dean–Stark apparatus, reflux condenser was charged with α-azido ketone **18** (14.0 mg, 0.016 mmol, 1.0 equiv), α-amino methoxime **21** (9.14 mg, 0.016 mmol, 1.0 equiv), Bu_2SnCl_2 (1.0 mg, 0.032 mmol, 20 mol %), polyvinylpyridine (28.0 mg, 200 wt %) and PhH (3.2 mL, 0.005 M). The flask was removed from the glovebox, equipped with a reflux condenser, placed in an oil bath preheated to 85 °C, and the resulting mixture was heated to reflux for 6 h. After cooling to room temperature, the reaction was filtered through a cotton plug and was concentrated in vacuo. The crude product was purified by flash column chromatography (20 to 30 to 40% EtOAc/hexanes) to afford pyrazine **S19** (12.7 mg, 0.01 mmol, 57% yield) as a colorless foam.[9]

TLC (40% Et_2O/hexanes): R_f = 0.42 (*p*-anisaldehyde)
^{1}H NMR (400 MHz, C_6D_6): δ 5.77 (t, *J* = 1.6 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.83 (t, *J* = 7.0 Hz, 1H), 4.21 (dd, *J* = 10.7, 5.2 Hz, 1H), 3.97 (td, *J* = 10.3, 4.9 Hz, 1H), 3.76 (d, *J* = 11.6 Hz, 1H), 3.43 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.32 – 3.27 (m, 2H), 3.24 – 3.12 (m, 3H), 2.97 (ddd, *J* = 18.1, 8.7, 5.5 Hz, 2H), 2.74 (dt, *J* = 15.2, 10.2 Hz, 3H), 2.67 – 2.53 (m, 4H), 2.31 (td, *J* = 13.0, 6.7 Hz, 2H), 2.24 (t, *J* = 7.4 Hz, 2H), 2.15 – 2.07 (m, 5H), 2.03 – 1.90 (m, 10H), 1.86 – 1.73 (m, 6H), 1.69 – 1.59 (m, 9H), 1.57 – 1.54 (m, 3H), 1.53 (d, *J* = 3.2 Hz, 2H), 1.50 (d, *J* = 3.1 Hz, 2H), 1.48 (d, *J* = 3.4 Hz, 2H), 1.47 – 1.44 (m, 7H), 1.43 – 1.41 (m, 3H), 1.41 – 1.38 (m, 4H), 1.37 – 1.36 (m, 6H), 1.35 (s, 3H), 1.34 (s, 6H), 1.33 – 1.31 (m, 7H), 1.31 – 1.29 (m, 7H), 1.28 – 1.26 (m, 6H), 1.22 (s, 6H), 1.20 (d, *J* = 2.7 Hz, 6H), 1.18 (s, 9H), 1.17 (d, *J* = 2.1 Hz, 9H), 1.15 (s, 3H), 1.13 (s, 6H), 1.08 (s, 4H), 1.06 (s, 9H), 1.03 (s, 12H), 1.01 (s, 9H), 1.00 (d, *J* = 1.2 Hz, 2H), 0.98 (s, 1H), 0.97 – 0.95 (m, 4H), 0.95 – 0.93 (m, 3H), 0.92 (s, 3H), 0.92 – 0.89 (m, 4H), 0.87 (s, 4H), 0.83 (dd, *J* = 11.7, 3.6 Hz, 3H), 0.80 – 0.77 (m, 1H), 0.73 (d, *J* = 5.2 Hz, 1H), 0.68 (s, 3H), 0.61 (s, 3H), 0.30 (s, 6H), 0.24 (s, 3H), 0.12 (s, 3H), 0.09 – 0.05 (m, 9H).
^{13}C NMR (101 MHz, C_6D_6): δ 151.28, 149.31, 149.16, 148.58, 148.28, 121.09, 116.86, 107.66, 94.79, 92.07, 81.65, 79.77, 74.56, 74.04, 71.59, 69.76, 69.68, 57.57, 56.46, 50.53, 49.01, 48.54, 47.71, 46.33, 45.89, 45.37, 43.39, 42.44, 41.54, 39.50, 38.65, 37.83, 35.74, 35.45, 34.25, 34.15, 33.60, 32.85, 32.50,

32.43, 32.37, 31.65, 30.82, 30.36, 30.23, 30.16, 29.86, 29.80, 29.58, 28.88, 28.78, 27.91, 26.44, 26.41, 26.23, 26.18, 23.15, 18.93, 18.90, 18.56, 18.50, 18.33, 14.89, 14.40, 13.84, 13.82, 13.60, 11.77, 11.76, 8.39, 1.42, -1.98, -2.14, -3.32, -3.51, -4.05, -4.69.
FTIR (NaCl, thin film, cm^{-1}): 3522, 2953, 2925, 1858, 1743, 1470, 1462, 1456, 1385, 1252, 1090 cm^{-1}.
HRMS (TOF-ESI, m/z): calc'd for $C_{81}H_{141}N_2O_9Si_4$: 1397.9714 $[M+H]^+$; found: 1397.9714.
$[\alpha]_D^{21}$: +28° (c = 0.083, CH_2Cl_2).

Preparation of ritterazine B (1):

A 10 mL round-bottom flask with a stir bar was charged with pyrazine **S19** (8.0 mg, 5.7 μmol, 1.0 equiv) and THF (2.3 mL 0.0025 M). The flask was equipped with a reflux condenser and TBAF (1.0 M in THF, 114 μL, 0.11 mmol, 20 equiv) was added. The reaction was placed in an oil bath pre-heated to 65 °C and was stirred at for 12 h. After cooling to room temperature, the reaction was concentrated, and the resulting residue taken up in EtOAc (1 mL) and washed with H_2O (8 × 1 mL). The organic layer was dried over anhydrous Na_2SO_4, concentrated in vacuo, and the crude product was purified by flash column chromatography (4 to 8 to 12% MeOH/DCM) to afford ritterazine B **(1)** (4.2 mg, 4.7 μmol, 82% yield) as a colorless glassy solid.[7]

TLC (7% MeOH/DCM): R_f = 0.36 (p-anisaldehyde)
^{1}H NMR (400 MHz, C_5D_5N): δ 6.16 (t, J = 1.7 Hz, 1H), 6.12 (d, J = 4.9 Hz, 1H), 5.87 (d, J = 5.0 Hz, 1H), 5.70 (s, 1H), 5.28 (d, J = 1.9 Hz, 1H), 4.81 (t, J = 6.8 Hz, 1H), 4.71 (d, J = 2.0 Hz, 1H), 4.27 – 4.19 (m, 1H), 4.13 – 4.06 (m, 1H), 4.04 (d, J = 11.4 Hz, 1H), 3.69 – 3.61 (m, 2H), 3.21 (d, J = 6.7 Hz, 1H), 3.19 – 3.14 (m, 2H), 2.98 (td, J = 18.0, 5.4 Hz, 2H), 2.85 – 2.77 (m, 1H), 2.77 – 2.71 (m, 2H), 2.71 – 2.64 (m, 1H), 2.57 – 2.49 (m, 1H), 2.47 – 2.41 (m, 1H), 2.27 – 2.16 (m, 4H), 2.14 (t, J = 3.6 Hz, 1H), 2.12 (s, 1H), 2.11 – 2.09 (m, 1H), 2.08 (s, 1H), 2.05 – 2.03 (m, 1H), 1.91 (s, 1H), 1.90 – 1.87 (m, 2H), 1.86 – 1.84 (m, 1H), 1.84 – 1.82 (m, 1H), 1.79 – 1.77 (m, 1H), 1.76 – 1.72 (m, 1H), 1.72 – 1.68 (m, 2H), 1.62 – 1.56 (m,

1H), 1.53 – 1.50 (m, 1H), 1.50 – 1.46 (m, 2H), 1.45 (s, 3H), 1.41 – 1.39 (s, 1H), 1.37 (s, 2H), 1.35 (s, 3H), 1.32 (d, J = 3.3 Hz, 1H), 1.29 (d, J = 7.0 Hz, 3H), 1.29 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H), 1.21 (d, J = 6.8 Hz, 3H), 1.18 – 1.16 (m, 1H), 1.15 – 1.12 (m, 1H), 1.11 – 1.07 (m, 1H), 0.87 (s, 3H), 0.77 (s, 3H).
^{13}C NMR (101 MHz, C_5D_5N): δ 152.01, 149.55, 149.23, 149.09, 148.74, 121.58, 117.43, 108.34, 94.39, 93.64, 81.81, 80.39, 76.17, 72.15, 70.57, 69.82, 66.15, 57.92, 56.51, 51.57, 49.01, 48.64, 48.18, 46.70, 46.30, 45.88, 43.24, 42.40, 41.94, 40.40, 38.83, 38.17, 36.31, 36.25, 36.03, 33.62, 33.61, 33.20, 33.03, 32.16, 31.15, 30.68, 29.60, 29.40, 29.16, 27.87, 27.38, 15.10, 14.13, 12.94, 12.31, 12.20, 8.49.
FTIR (NaCl, thin film, cm^{-1}): 3444, 2920, 2854, 2352, 2333, 1667, 1455, 1397, 1262, 1045, 1034 cm^{-1}.
HRMS (TOF-ESI, m/z): calc'd for $C_{54}H_{79}N_2O_9$: 899.5786 $[M+H]^+$; found: 899.5781.
$[\alpha]_D^{21}$: +31° (c = 0.250, CH_2Cl_2).

Note: NMR chemical shift references for C_5D_5N vary by source. There is no information on the reference shift used in the isolation report from Fusetani et al.[10] Herein, the reference shifts provided by Cambridge Isotope Laboratories, Inc., from whom our C_5D_5N was purchased, are used. For ^{1}H NMR: 8.74, 7.58, 7.22. For ^{13}C NMR: 150.35, 135.91, 123.87. These values lead to a consistent shift of 0.04 ppm in ^{1}H NMR and 0.4 ppm in ^{13}C NMR between our chemical shifts (at 297K) and those from Fusetani (at 303K). Raw Δδ and those normalized for this shift (norm) are presented below.

Table S4. Comparison of spectroscopic data for natural (Fusetani)[10] and synthetic (Reisman) ritterazine B (1)

western half				
proton	natural (Fusetani)	synthetic (Reisman)	Δδ	norm. Δδ (–0.04)
1α'	2.68	2.71	0.03	-0.01
1β'	3.15	3.18	0.03	-0.01
4α'	2.98	3.01	0.03	-0.01
4β'	2.77	2.81	0.04	0.00
5'	1.84	1.86	0.02	-0.02
6α'	2.18	2.21	0.03	-0.01
6β'	1.76	1.78	0.02	-0.02
7'	4.06	4.09	0.03	-0.01
8'	2.41	2.45	0.04	0.00
9'	1.16	1.18	0.02	-0.02
11α'	2.17	2.20	0.03	-0.01
11β'	1.88	1.91	0.03	-0.01
12'	4.20	4.24	0.04	0.00
15'	6.13	6.16	0.03	-0.01
16'	5.25	5.28	0.03	-0.01
18'	1.33	1.36	0.03	-0.01
19'	0.85	0.87	0.02	-0.02
20'	2.21	2.24	0.03	-0.01
21'	1.26	1.29	0.03	-0.01
23α'	2.50	2.54	0.04	0.00
23β'	1.49	1.52	0.03	-0.01
24α'	1.87	1.90	0.03	-0.01
24β'	2.16	2.19	0.03	-0.01
26α'	3.61	3.64	0.03	-0.01
26β'	4.02	4.04	0.02	-0.02
27'	1.22	1.26	0.04	0.00
7'-OH	–	6.12	–	–
12'-OH	4.67	4.71	0.04	0.00
17'-OH	–	5.70	–	–
25'-OH	3.69	3.70	0.01	-0.03

eastern half				
proton	natural (Fusetani)	synthetic (Reisman)	Δδ	norm. Δδ (–0.04)
1α	2.71	2.75	0.04	0.00
1β	3.17	3.21	0.04	0.00
4α	2.94	2.98	0.04	0.00
4β	2.68	2.72	0.04	0.00
5	1.57	1.60	0.03	-0.01
6α	1.48	1.49	0.01	-0.03
6β	1.28	1.32	0.04	0.00
7α	1.10	1.14	0.04	0.00
7β	1.49	1.50	0.01	-0.03
8	1.68	1.71	0.03	-0.01
9	1.36	1.39	0.03	-0.01
11α	2.04	2.08	0.04	0.00
11β	1.67	1.68	0.01	-0.03
12	3.64	3.67	0.03	-0.01
14	2.08	2.12	0.04	0.00
15α	1.80	1.82	0.02	-0.02
15β	1.83	1.84	0.01	-0.03
16	4.78	4.81	0.03	-0.01
17	3.15	3.18	0.03	-0.01
18	1.26	1.29	0.03	-0.01
19	0.75	0.77	0.02	-0.02
20	2.01	2.04	0.03	-0.01
21	1.18	1.21	0.03	-0.01
23α	1.85	1.88	0.03	-0.01
23β	2.12	2.14	0.02	-0.02
24α	1.68	1.70	0.02	-0.02
24β	2.04	2.10	0.06	0.02
26	1.18	1.21	0.03	-0.01
27	1.43	1.45	0.02	-0.02
12-OH	5.80	5.87	0.07	0.03

western half				
carbon	natural (Fusetani)	synthetic (Reisman)	Δδ	norm. Δδ (–0.4)
1'	45.9	46.3	0.4	0.0
2'	148.6	149.1	0.5	0.1
3'	148.1	148.7	0.6	0.2
4'	35.6	36.0	0.4	0.0
5'	40.0	40.4	0.4	0.0
6'	38.4	38.8	0.4	0.0
7'	69.4	69.8	0.4	0.0
8'	42.8	43.2	0.4	0.0
9'	51.2	51.6	0.4	0.0
10'	35.9	36.2	0.3	-0.1
11'	29.2	29.6	0.4	0.0
12'	75.6	76.2	0.6	0.2
13'	56.1	56.5	0.4	0.0
14'	151.6	152.0	0.4	0.0
15'	121.1	121.6	0.5	0.1
16'	94.0	94.4	0.4	0.0
17'	93.3	93.6	0.3	-0.1
18'	12.5	12.9	0.4	0.0
19'	11.5	12.2	0.7	0.3
20'	48.2	48.6	0.4	0.0
21'	8.1	8.5	0.4	0.0
22'	107.9	108.3	0.4	0.0
23'	27.5	27.9	0.4	0.0
24'	33.2	33.6	0.4	0.0
25'	65.8	66.2	0.4	0.0
26'	70.2	70.6	0.4	0.0
27'	27.0	27.4	0.4	0.0

eastern half				
carbon	natural (Fusetani)	synthetic (Reisman)	Δδ	norm. Δδ (–0.4)
1	46.3	46.7	0.4	0.0
2	149.3	149.6	0.3	-0.1
3	149.0	149.2	0.2	-0.2
4	35.9	36.3	0.4	0.0
5	41.5	41.9	0.4	0.0
6	29.0	29.4	0.4	0.0
7	31.7	32.2	0.5	0.1
8	32.6	33.0	0.4	0.0
9	45.5	45.9	0.4	0.0
10	35.9	36.3	0.4	0.0
11	30.7	31.2	0.5	0.1
12	71.8	72.2	0.4	0.0
13	48.6	49.0	0.4	0.0
14	47.8	48.2	0.4	0.0
15	32.8	33.2	0.4	0.0
16	80.0	80.4	0.4	0.0
17	57.5	57.9	0.4	0.0
18	13.7	14.1	0.4	0.0
19	11.9	12.3	0.4	0.0
20	42.0	42.4	0.4	0.0
21	14.7	15.1	0.4	0.0
22	117.0	117.4	0.4	0.0
23	33.2	33.6	0.4	0.0
24	37.3	38.2	0.9	0.5
25	81.4	81.8	0.4	0.0
26	28.8	29.2	0.4	0.0
27	30.3	30.7	0.4	0.0

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4. ^{1}H and ^{13}C NMR spectral data

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ TO-1-125-C13/ 1/ fid
Title	TO-1-125-C13.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-10-19T09:49:36
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1638.5
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S1

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ TO-1-125-C13/ 2/ fid
Title	TO-1-125-C13.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	38.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-10-19T10:10:47
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S1

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-2-086/ 3/ fid
Title	MRM-2-086.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2019-01-15T21:05:31
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

9

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-2-086/ 2/ fid
Title	MRM-2-086.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-01-15T11:02:22
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1936.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

9

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-085-main/ 1/ fid
Title	MRM-3-085-main.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-08-17T09:25:21
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.7
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

10

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-085-main/ 2/ fid
Title	MRM-3-085-main.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-17T09:46:32
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

10

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-085-main/ 4/ ser
Title	MRM-3-085-main.4.ser
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	hsqcedetgpsisp2.4
Number of Scans	2
Receiver Gain	197.4
Relaxation Delay	1.5000
Pulse Width	12.5000
Acquisition Time	0.2135
Acquisition Date	2020-08-17T09:47:48
Spectrometer Frequency	(400.13, 100.62)
Spectral Width	(4795.4, 16611.3)
Lowest Frequency	(-527.2, -1265.3)
Nucleus	(1H, 13C)
Acquired Size	(1024, 180)
Spectral Size	(1024, 1024)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-085-main/ 6/ ser
Title MRM-3-085-main.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-08-17T21:51:43
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.2, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
O
Me
H
Br
H
H
TBSO
10
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-085-main/ 8/ ser
Title MRM-3-085-main.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-08-17T22:36:16
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.2, -168.2)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
O
Me
H
Br
H
H
TBSO
10
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-086-main/ 1/ fid
Title	MRM-3-086-main.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-08-20T12:44:47
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.6
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S2a

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-086-main/ 2/ fid
Title	MRM-3-086-main.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-20T13:06:35
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S2a

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-2-088-1/ 1/ fid
Title	MRM-2-088-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2019-01-21T15:00:38
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

S2a

S2b

1 : 1

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-2-088-1/ 2/ fid
Title	MRM-2-088-1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-01-21T15:22:21
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1946.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S2a

S2b

1 : 1

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-045-2D/ 1/ fid
Title	YN-3-045-2D.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-08-28T10:53:44
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.6
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

11

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-045-2D/ 2/ fid
Title	YN-3-045-2D.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-28T11:14:55
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1944.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

11

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-079-main/ 1/ fid
Title	MRM-3-079-main.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-08-25T08:15:23
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.6
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

12

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-079-main/ 2/ fid
Title	MRM-3-079-main.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-25T08:36:35
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

12

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-079-main/ 4/ ser
Title MRM-3-079-main.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-08-25T08:37:51
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.1, -1265.3)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
O
Me
H
OH
H
TBSO
12
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-079-main/ 8/ ser
Title MRM-3-079-main.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-08-25T08:55:07
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.1, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
O
Me
H
OH
H
TBSO
12
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-079-main/ 10/ ser
Title MRM-3-079-main.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-08-25T21:04:37
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.1, -168.1)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
O
Me
H
OH
H
TBSO
12
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-091/ 1/ fid
Title	MRM-2-091.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2019-03-07T17:05:45
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

S3

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-091/ 2/ fid
Title	MRM-2-091.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-03-07T17:26:58
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1948.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S3

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-092-110120/ 1/ fid
Title	MRM-2-092-110120.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-11-01T08:42:45
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S4

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-092-110120/ 2/ fid
Title	MRM-2-092-110120.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-11-01T09:04:42
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S4

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-044/ 1/ fid
Title	YN-3-044.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-08-26T07:35:03
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.6
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S5

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-044/ 2/ fid
Title	YN-3-044.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	38.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-26T07:58:37
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S5

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-116/ 1/ fid
Title	MRM-3-116.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-12-13T08:38:54
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

S6

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-116/ 2/ fid
Title	MRM-3-116.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-12-13T09:00:05
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1947.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S6

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-066-check/ 1/ fid
Title	YN-3-066-check.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-01-27T16:41:25
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

6

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-066-check-C13/ 1/ fid
Title	YN-3-066-check-C13.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-01-29T08:10:13
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

6

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ yasuaki/ vnmrsys/ data/ YN-2-268/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	40
Relaxation Delay	2.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2018-08-04T16:05:30
Spectrometer Frequency	499.64
Spectral Width	8000.0
Lowest Frequency	-1030.2
Nucleus	1H
Acquired Size	24000
Spectral Size	65536

S7

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-046/ 2/ fid
Title	YN-3-046.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-26T08:25:47
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1946.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S7

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-052-reiso/ 1/ fid
Title	YN-3-052-reiso.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-03-12T07:30:13
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

7

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-052-reiso/ 2/ fid
Title	YN-3-052-reiso.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-03-12T07:51:59
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

7

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-090/ 1/ fid
Title	MRM-3-090.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-08-27T11:21:50
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.6
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

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Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-090/ 2/ fid
Title	MRM-3-090.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-27T11:43:04
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

13

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-090/ 4/ ser
Title MRM-3-090.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-08-27T22:53:56
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.1, -1265.3)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
Me
OH
OH
Me
H
H
TBSO
Me
Me
OTBS
OPMP
13
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-090/ 6/ ser
Title MRM-3-090.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 43.7
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-08-27T23:05:21
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-208.0, -208.0)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
Me
Me
Me
H
H
OH
OH
Me
OTBS
OPMP
TBSO
13
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-090/ 8/ ser
Title MRM-3-090.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-08-27T23:11:12
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.1, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
Me
OH
OH
Me
H
H
TBSO
Me
OTBS
OPMP
13
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-090/ 10/ ser
Title MRM-3-090.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-08-27T23:55:40
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.1, -168.1)
Nucleus (1H,1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
Me
OH
OH
Me
H
H
TBSO
Me
Me
OTBS
OPMP
13
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-060-122220/ 1/ fid
Title	YN-3-060-122220.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-12-22T09:55:08
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-060-122220/ 2/ fid
Title	YN-3-060-122220.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-12-22T10:39:39
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-3-060-2D/ 6/ ser
Title YN-3-060-2D.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-08-31T09:31:46
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.2, -1265.3)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
Me
OH
O
Me
H
H
TBSO
Me
OTBS
OPMP
S8
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-3-060-2D/ 8/ ser
Title YN-3-060-2D.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-08-31T09:43:18
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.3, -1119.0)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
Me
OH
O
Me
H
H
TBSO
Me
Me
OTBS
OPMP
S8
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-092/ 1/ fid
Title	MRM-3-092.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-08T11:50:57
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

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Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-092/ 2/ fid
Title	MRM-3-092.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-08T12:12:13
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-094/ 12/ fid
Title	MRM-3-094.12.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	32
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-16T13:42:21
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1636.7
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-094/ 2/ fid
Title	MRM-3-094.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-16T06:49:37
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-094/ 6/ ser
Title MRM-3-094.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-09-16T06:56:34
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.8, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
Me
OH
OH
Me
H
H
TBSO
Me
OTBS
OH
4
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-094/ 8/ ser
Title MRM-3-094.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-09-16T07:08:06
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-172.9, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
Me
OH
OH
Me
H
H
TBSO
Me
OTBS
OH
4
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-094/ 10/ ser
Title MRM-3-094.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 35.5
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-09-16T07:52:39
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-167.9, -167.9)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
Me
OH
OH
Me
H
H
TBSO
4
Me
OTBS
OH
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-2-256-2D-2/ 1/ fid
Title	YN-2-256-2D-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-01T06:45:43
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.5
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-2-256-2D-2/ 2/ fid
Title	YN-2-256-2D-2.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-01T07:07:37
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-2-256-2D/ 4/ ser
Title YN-2-256-2D.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 64.2
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-08-31T07:24:29
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-207.9, -207.9)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
O
H
15
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-2-256-2D-2/ 4/ ser
Title YN-2-256-2D-2.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-09-01T07:08:52
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.0, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
O
H
15
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-2-256-2D/ 8/ ser
Title YN-2-256-2D.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-08-31T07:30:20
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.0, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
HO
Me
OTBS
H
O
15
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-2-256-2D/ 10/ ser
Title YN-2-256-2D.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-08-31T08:14:48
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.0, -168.0)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
H
O
15
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-050-2D/ 1/ fid
Title	MRM-3-050-2D.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-07T06:51:28
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S10

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-050-2D/ 2/ fid
Title	MRM-3-050-2D.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-07T07:12:40
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-050-2D/ 6/ ser
Title MRM-3-050-2D.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-09-07T07:19:31
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
O
H
S10
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-050-2D/ 8/ ser
Title MRM-3-050-2D.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-09-07T07:31:03
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-163.1, -1116.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
HO
Me
OTBS
H
O
S10
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-top/ 1/ fid
Title	MRM-2-106-repurify-top.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-09T12:07:17
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-top/ 2/ fid
Title	MRM-2-106-repurify-top.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-09T12:28:28
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-top/ 4/ ser
Title MRM-2-106-repurify-top.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 21.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-09-09T12:29:26
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-207.8, -207.8)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
HO
Me
Me
Me
OTBS
O
O
H
H
H
H
TBSO
OH
16
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-top/ 6/ ser
Title MRM-2-106-repurify-top.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-09-09T21:18:20
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.9, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
O
H
OH
16
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-top/ 8/ ser
Title MRM-2-106-repurify-top.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-09-09T21:29:52
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-172.9, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
HO
Me
OTBS
O
H
OH
16
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-top/ 10/ ser
Title MRM-2-106-repurify-top.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 35.5
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-09-09T22:14:25
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.0, -168.0)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
O
H
OH
16
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-bottom/ 1/ fid
Title	MRM-2-106-repurify-bottom.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-09T12:38:48
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S11

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-bottom/ 2/ fid
Title	MRM-2-106-repurify-bottom.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-09T13:00:01
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S11

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-bottom/ 6/ ser
Title MRM-2-106-repurify-bottom.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-09-09T23:03:01
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.9, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
Me
OTBS
Me
HO
TBSO
Me
O
Me
H
O
H
H
H
TBSO
OH
H
S11
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-bottom/ 8/ ser
Title MRM-2-106-repurify-bottom.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-09-09T23:14:33
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-172.9, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
Me
OTBS
Me
HO
TBSO
Me
O
O
Me
H
H
H
H
TBSO
OH
H
S11
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-106-repurify-bottom/ 10/ ser
Title MRM-2-106-repurify-bottom.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-09-09T23:59:01
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-167.9, -167.9)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
O
H
OH
S11
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-095/ 1/ fid
Title	MRM-3-095.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-22T09:06:58
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.3
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

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Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-095/ 2/ fid
Title	MRM-3-095.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-22T09:48:51
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-103/ 1/ fid
Title	MRM-3-103.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-11-02T09:41:33
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-103/ 2/ fid
Title	MRM-3-103.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-11-02T10:34:30
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-103/ 6/ ser
Title MRM-3-103.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-11-02T21:06:19
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
OTIPS
2
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-103/ 8/ ser
Title MRM-3-103.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-11-02T21:17:52
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-163.1, -1116.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
Me
OTBS
TBSO
HO
Me
Me
O
Me
H
O
H
H
O
OTIPS
2
H
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-105/ 1/ fid
Title	MRM-3-105.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-11-04T09:06:05
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-105/ 2/ fid
Title	MRM-3-105.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-11-04T09:47:58
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1944.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-105/ 6/ ser
Title MRM-3-105.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-11-05T00:38:29
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.9, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
Me
OTBS
Me
HO
TBSO
Me
O
O
Me
H
Br
H
H
O
H
OTIPS
S12
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-105/ 8/ ser
Title MRM-3-105.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-11-05T00:50:02
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-172.9, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
Me
OTBS
Me
HO
TBSO
Me
O
O
Me
H
Br
H
H
O
H
OTIPS
S12
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-105/ 10/ ser
Title MRM-3-105.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-11-05T01:34:40
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.0, -168.0)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
Br
O
Me
H
TBSO
Me
HO
Me
Me
OTBS
O
O
H
OTIPS
S12
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-109/ 1/ fid
Title	MRM-3-109.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-12-01T14:08:35
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.7
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-109/ 2/ fid
Title	MRM-3-109.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-12-01T21:45:21
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1944.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-109/ 6/ ser
Title MRM-3-109.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-12-01T21:52:12
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.1, -1265.3)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
N3
OTIPS
18
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-109/ 8/ ser
Title MRM-3-109.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-12-01T22:03:45
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.2, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
Me
OTBS
TBSO
HO
Me
Me
O
O
Me
H
N3
H
H
O
H
OTIPS
18
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-109/ 10/ ser
Title MRM-3-109.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 87.8
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-12-01T22:48:32
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.2, -168.2)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
HO
Me
OTBS
N3
OTIPS
18
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-089/ 1/ fid
Title	MRM-3-089.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-08-27T10:55:07
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.7
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-089/ 2/ fid
Title	MRM-3-089.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-27T11:16:18
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1944.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-089/ 6/ ser
Title MRM-3-089.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 38.0
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-08-27T21:16:16
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-198.0, -198.0)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
Me
Me
OH
OH
TMSO
Me
Me
Me
H
H
TBSO
14
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-089/ 4/ ser
Title MRM-3-089.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-08-27T21:04:51
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
Me
OH
OH
TMSO
Me
Me
Me
H
H
TBSO
14
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-089/ 8/ ser
Title MRM-3-089.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-08-27T21:22:07
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-163.1, -1116.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
Me
OH
OH
TMSO
Me
Me
Me
H
H
TBSO
14
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-089/ 10/.ser
Title MRM-3-089.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-08-27T22:06:35
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-158.1, -158.1)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
Me
OH
OH
TMSO
Me
Me
Me
H
H
TBSO
14
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-099/ 2/ fid
Title	MRM-2-099.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2019-03-27T09:23:47
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1568.7
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

S13

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-2-099/ 3/ fid
Title	MRM-2-099.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-03-27T09:45:35
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S13

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-091-2D/ 1/ fid
Title	MRM-3-091-2D.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-08T07:31:28
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

19

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-096/ 2/ fid
Title	MRM-3-096.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-24T08:54:58
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ yasuaki/ vnmrsys/ data/ YN-3-025/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	36
Relaxation Delay	2.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2018-12-04T19:23:19
Spectrometer Frequency	499.63
Spectral Width	8000.0
Lowest Frequency	-1014.4
Nucleus	1H
Acquired Size	24000
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-107/ 2/ fid
Title	MRM-3-107.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-11-30T00:16:31
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S14

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-107/ 4/ ser
Title MRM-3-107.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 64.2
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-11-30T00:17:24
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-198.0, -198.0)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
Me
Me
H
Me
Me
HO
Me
H
O
H
TBSO
S14
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-107/ 6/ ser
Title MRM-3-107.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-11-30T00:23:22
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
Me
H
Me
Me
HO
Me
H
O
H
TBSO
S14
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-107/ 8/ ser
Title MRM-3-107.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-11-30T00:34:54
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-163.1, -1116.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
Me
H
Me
H
H
O
TBSO
Me
Me
HO
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-107/ 10/ ser
Title MRM-3-107.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 112.8
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-11-30T01:19:30
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-158.1, -158.1)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
Me
H
Me
Me
HO
Me
H
O
H
TBSO
S14
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ yasuaki/ vnmrsys/ data/ YN-3-026/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	30
Relaxation Delay	2.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2018-12-04T23:10:56
Spectrometer Frequency	499.63
Spectral Width	8000.0
Lowest Frequency	-1014.5
Nucleus	1H
Acquired Size	24000
Spectral Size	65536

5

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-111/ 11/ fid
Title	MRM-3-111.11.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	2048
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-12-03T08:04:40
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1944.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-111/ 4/ ser
Title MRM-3-111.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 112.8
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-12-02T23:18:28
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-198.0, -198.0)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
Me
Me
H
OH
HO
Me
Me
Me
H
H
TBSO
5
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ MRM-3-111/ 10/ ser
Title MRM-3-111.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-12-03T00:20:31
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-158.1, -158.1)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
Me
H
OH
HO
Me
Me
Me
H
H
TBSO
5
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-074-2D/ 1/ fid
Title	YN-3-074-2D.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-01T07:25:08
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.5
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

20

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ mmaser/ nmr/ YN-3-074-2D/ 2/ fid
Title	YN-3-074-2D.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-01T07:46:22
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

20

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-3-074-2D/ 4/ ser
Title YN-3-074-2D.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 38.0
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-09-01T07:47:22
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-207.9, -207.9)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
Me
H
Me
Me
Me
O
O
H
Me
H
H
HO
20
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-3-074-2D/ 6/ ser
Title YN-3-074-2D.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-09-01T07:53:20
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.0, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
H
Me
Me
Me
O
O
H
Me
H
H
HO
20
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-3-074-2D/ 8/ ser
Title YN-3-074-2D.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-09-01T08:50:34
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.0, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
H
O
HO
20
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata/ mmaser/ nmr/ YN-3-074-2D/ 10/ ser
Title YN-3-074-2D.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-09-01T09:42:56
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.0, -168.0)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
H
Me
Me
Me
O
O
H
Me
H
H
HO
20
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-097-main/ 1/ fid
Title	MRM-3-097-main.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-10-19T10:25:13
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S15

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-097-main/ 2/ fid
Title	MRM-3-097-main.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-10-19T21:38:40
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S15

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-097-main/ 4/ ser
Title MRM-3-097-main.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 38.0
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-10-19T21:39:40
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-207.8, -207.8)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
Me
H
O
HO
S15
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-097-main/ 6/ ser
Title MRM-3-097-main.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-10-19T21:45:38
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-526.9, -1265.2)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
H
O
HO
S15
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-097-main/ 8/ ser
Title MRM-3-097-main.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-10-19T21:57:11
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-172.9, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
HO
Me
H
O
S15
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-097-main/ 10/ ser
Title MRM-3-097-main.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-10-19T22:41:39
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.0, -168.0)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
H
O
HO
S15
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-2-146-2D/ 1/ fid
Title	MRM-2-146-2D.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-09-01T12:35:11
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.5
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-2-146-2D/ 2/ fid
Title	MRM-2-146-2D.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-09-01T21:30:13
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-087/ 1/ fid
Title	MRM-3-087.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-08-20T06:25:24
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.6
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S16

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-087/ 2/ fid
Title	MRM-3-087.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-08-20T06:46:35
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-087/ 4/ ser
Title MRM-3-087.4.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-08-20T06:47:50
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-527.1, -1265.3)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Br
Me
H
O
S16
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-087/ 6/ ser
Title MRM-3-087.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-08-20T06:59:22
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-173.2, -1118.9)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Br
O
Me
H
S16
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-087.8/ ser
Title MRM-3-087.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-08-20T07:43:50
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.2, -168.2)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
H
Br
O
S16
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-099-main/ 1/ fid
Title	MRM-3-099-main.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	2.8224
Acquisition Date	2020-10-25T08:12:02
Spectrometer Frequency	400.13
Spectral Width	11609.9
Lowest Frequency	-1613.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

S17

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-099-main/ 2/ fid
Title	MRM-3-099-main.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-10-25T08:54:34
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-099-main/ 10/ ser
Title MRM-3-099-main.10.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 112.8
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-10-25T12:00:33
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-168.0, -168.0)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
H
O
N3
S17
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-106/ 1/ fid
Title	MRM-3-106.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	32
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-11-29T09:47:16
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1546.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-106/ 2/ fid
Title	MRM-3-106.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-11-29T21:44:52
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1944.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-106/ 6/ ser
Title MRM-3-106.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-11-29T21:51:46
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
H
O
N3
N
OMe
S18
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-106/ 8/ ser
Title MRM-3-106.8.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-11-29T22:03:19
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-163.1, -1116.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
H
N3
N
OMe
O
S18
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-110/ 1/ fid
Title	MRM-3-110.1.fid
Origin	Bruker BioSpin GmbH
Solvent	C6D6
Temperature	297.2
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-12-01T14:13:56
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1492.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-110 2/ fid
Title	MRM-3-110.2.fid
Origin	Bruker BioSpin GmbH
Solvent	C6D6
Temperature	297.2
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-12-02T00:18:25
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-2042.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-110/ 4/ ser
Title MRM-3-110.4.ser
Origin Bruker BioSpin GmbH
Solvent C6D6
Temperature 297.1
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 50.3
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-12-02T00:19:27
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-198.0, -198.0)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
TBSO
Me
H
O
H2N
N
OMe
21
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-110/ 6/ ser
Title MRM-3-110.6.ser
Origin Bruker BioSpin GmbH
Solvent C6D6
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-12-02T00:25:24
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
TBSO
Me
H
Me
Me
Me
O
O
H
H
H

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-110/ 8/ ser
Title MRM-3-110.8.ser
Origin Bruker BioSpin GmbH
Solvent C6D6
Temperature 297.1
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-12-02T00:36:57
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-163.1, -1116.4)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
TBSO
Me
H
O
H2N
N
OMe
21
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-110/ 10/ ser
Title MRM-3-110.10.ser
Origin Bruker BioSpin GmbH
Solvent C6D6
Temperature 297.2
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 64.2
Relaxation Delay 1.8000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-12-02T01:21:25
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-158.1, -158.1)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TBSO
Me
H
O
H2N
N
OMe
21
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-112-122220/ 1/ fid
Title	MRM-3-112-122220.1.fid
Origin	Bruker BioSpin GmbH
Solvent	C6D6
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	64
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-12-22T10:58:09
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1532.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-112-122220/ 2/ fid
Title	MRM-3-112-122220.2.fid
Origin	Bruker BioSpin GmbH
Solvent	C6D6
Temperature	297.1
Pulse Sequence	zgpg30
Number of Scans	5120
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2020-12-23T04:03:32
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1922.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter
Value
Data File Name
/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-112/ 4/ ser
Title
MRM-3-112.4.ser
Origin
Bruker BioSpin GmbH
Solvent
C6D6
Temperature
297.1
Pulse Sequence
cosygpppqf
Number of Scans
1
Receiver Gain
98.9
Relaxation Delay
2.0000
Pulse Width
12.5000
Acquisition Time
0.1970
Acquisition Date
2020-12-04T05:09:57
Spectrometer Frequency
(400.13, 400.13)
Spectral Width
(5197.5, 5197.5)
Lowest Frequency
(-198.0, -198.0)
Nucleus
(1H, 1H)
Acquired Size
(1024, 128)
Spectral Size
(1024, 1024)
S19
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-112/ 6/ ser
Title MRM-3-112.6.ser
Origin Bruker BioSpin GmbH
Solvent C6D6
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-12-04T05:15:54
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-517.1, -1262.8)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
S19
f2 (ppm)
f1 (ppm)

Parameter
Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-112/ 10/ ser
Title MRM-3-112.10.ser
Origin Bruker BioSpin GmbH
Solvent C6D6
Temperature 297.1
Pulse Sequence noesyphpp.2
Number of Scans 4
Receiver Gain 112.8
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.2560
Acquisition Date 2020-12-04T06:11:52
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-119.4, -119.4)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
TIPSO
TBSO
OTBS
OH
S19
f2 (ppm)
f1 (ppm)

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-039-2D/ 11/ fid
Title	MRM-3-039-2D.11.fid
Origin	Bruker BioSpin GmbH
Solvent	Pyr
Temperature	297.1
Pulse Sequence	zg30
Number of Scans	64
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Acquisition Date	2020-12-03T08:13:44
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1527.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ mmasey/ nmr/ MRM-2-133-4/ 2/ fid
Title	MRM-2-133-4.2.fid
Origin	Bruker BioSpin GmbH
Solvent	Pyr
Temperature	296.2
Pulse Sequence	zgpg30
Number of Scans	2048
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2019-06-15T09:49:04
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1895.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-039-2D/ 4/ ser
Title MRM-3-039-2D.4.ser
Origin Bruker BioSpin GmbH
Solvent Pyr
Temperature 297.1
Pulse Sequence cosygpppqf
Number of Scans 1
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.1970
Acquisition Date 2020-12-03T01:51:21
Spectrometer Frequency (400.13, 400.13)
Spectral Width (5197.5, 5197.5)
Lowest Frequency (-189.7, -189.7)
Nucleus (1H, 1H)
Acquired Size (1024, 128)
Spectral Size (1024, 1024)
ritterazine B (1)
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ hmrdata-1/ mmaser/ nmr/ MRM-3-039-2D/ 6/ ser
Title MRM-3-039-2D.6.ser
Origin Bruker BioSpin GmbH
Solvent Pyr
Temperature 297.1
Pulse Sequence hsqcedetgpsisp2.4
Number of Scans 2
Receiver Gain 197.4
Relaxation Delay 1.5000
Pulse Width 12.5000
Acquisition Time 0.2135
Acquisition Date 2020-12-03T01:57:19
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4795.4, 16611.3)
Lowest Frequency (-508.8, -1260.7)
Nucleus (1H, 13C)
Acquired Size (1024, 180)
Spectral Size (1024, 1024)
ritterazine B (1)
f2 (ppm)
f1 (ppm)

Parameter Value
Data File Name / Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-039-2D/ 8/ ser
Title MRM-3-039-2D.8.ser
Origin Bruker BioSpin GmbH
Solvent Pyr
Temperature 297.2
Pulse Sequence hmbcetgpl3nd
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 12.5000
Acquisition Time 0.4260
Acquisition Date 2020-12-03T02:08:51
Spectrometer Frequency (400.13, 100.62)
Spectral Width (4807.7, 22321.4)
Lowest Frequency (-154.9, -1114.3)
Nucleus (1H, 13C)
Acquired Size (2048, 256)
Spectral Size (2048, 1024)
ritterazine B (1)
f2 (ppm)
f1 (ppm)

Parameter
Value
Data File Name
/ Volumes/ nmrdata-1/ mmaser/ nmr/ MRM-3-039-2D/ 12/ ser
Title
MRM-3-039-2D.12.ser
Origin
Bruker BioSpin GmbH
Solvent
Pyr
Temperature
297.1
Pulse Sequence
roesyphpp.2
Number of Scans
4
Receiver Gain
112.8
Relaxation Delay
2.0123
Pulse Width
12.5000
Acquisition Time
0.2437
Acquisition Date
2020-12-03T08:15:32
Spectrometer Frequency
(400.13, 400.13)
Spectral Width
(4201.7, 4201.7)
Lowest Frequency
(-271.7, -271.7)
Nucleus
(1H, 1H)
Acquired Size
(1024, 256)
Spectral Size
(1024, 1024)
ritterazine B (1)
f2 (ppm)
f1 (ppm)